

BIOGEOCHEMISTRY OF MERCURY IN AN IMPACTED GOLD MINING  
TROPICAL AQUATIC SYSTEM: THE PRA RIVER BASIN IN SOUTHWESTERN  
GHANA

By

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TO MY LORD BE THE GLORY

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BIOGEOCHEMISTRY OF MERCURY IN AN IMPACTED GOLD MINING TROPICAL  
AQUATIC SYSTEM: THE PRA RIVER BASIN IN SOUTHWESTERN GHANA

By

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Chair: Jean-Claude J Bonzongo

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Artisanal gold mining (AGM) with metallic mercury ( $\text{Hg}^0$ ) has a long history in Ghana. It is believed to be over 2000 years old. Today, AGM in Ghana has escalated into a new dimension consuming about half of the country, thanks to its legalization by the government in 1989. This study investigated contamination levels and fate of mercury (Hg) in one of the 3 major river systems draining the gold-rich southwestern portion of Ghana, where gold is extracted primarily by the Hg amalgamation technique. Samples of water, sediment, soil and biota (i.e., human hair and fish) were collected from locations within the Pra River basin during the rainy and dry seasons of 2002 and 2003. Collected samples were: (1) analyzed for different Hg species and other trace metals (e.g. As, Pb, V, Cr, Ni, and Zn); and (2) used in controlled laboratory experiments to assess the fate of Hg introduced into the Pra River system by gold mining activities. In the aqueous phase, the average total-Hg (THg) concentration remained nearly constant regardless of the season ( $\sim 161 \text{ ng Hg L}^{-1}$ ), while the average methyl-Hg (MeHg) levels increased from

0.42 to 2.37 ng as Hg L<sup>-1</sup> from the dry to the wet season. THg and MeHg concentrations in soil and sediment spanned a broad range of values and increased from the dry to the wet season. On the other hand, AGM seemed to have a little impact on ambient levels of other trace metals. Overall, Hg levels and speciation in the studied aquatic system were controlled by the wet/dry cycles, which drive the hydrology and dictate differences in flow regimes versus seasons. Analysis of the few fish samples obtained indicated that Hg had entered the food chain, and in contrast to water, soil and sediment, Hg measured in hair samples collected during the dry period, which is the period of intense fishing, was higher than obtained on samples collected during the wet period.

Laboratory experiments assessing the fate of Hg introduced into the Pra River system by AGM focused primarily on the ability of both soil and sediment to produce and accumulate MeHg, the most toxic and readily bio-available Hg species in natural systems. These experiments led to the following conclusions: (1) soil hydration plays a key role in MeHg production in soils. Therefore, the rainy season would correspond to the time of high MeHg production in soils. Produced MeHg would then enter both surface- and ground-water by surface runoff and infiltration, respectively; (2) sediments in the Pra river basin do have a high potential to produce and accumulate MeHg, hence the potential to funnel Hg into the food chain; and (3) solar radiation is likely to exacerbate the production of Hg released in aqueous systems by AGM operations by making Hg previously bound to recalcitrant high molecular weight organic matter more accessible to methylating microbes.

Although AGM has been practiced in the Pra River basin for centuries, measured THg levels in different environmental compartments are rather low when compared to

other aquatic systems impacted by gold mining worldwide. This may be due to the self-cleansing nature of the river throughout the seasons. Accordingly, most of the Hg introduced into the river is likely transported to downstream terminal depositional basins, the river delta and the Gulf of Guinea. This last aspect is of concern as intense commercial fishing takes place in these basins.

## CHAPTER 1

### GENERAL INTRODUCTION

The mining of gold by the mercury (Hg) amalgamation technology has been known since ancient times. Because of the lack of innovations in prehistoric times, the amalgamation technique was the generally accepted procedure for the extraction of gold (Nriagu, 1994; Nriagu and Wong, 1997). With time, it became a unique and improved methodology along with panning and sluicing to retain the gold. New Spain (now Mexico) developed the Patio amalgamation process into commercial scale for recovery of gold and silver leading to increased demand for Hg. Subsequently, the entire world, particularly those of the developed nations in North America and Europe, adopted this technique as the only means to retrieve pure gold before its abandonment in the 1990s (Nriagu, 1994; Nriagu and Wong, 1997). As a consequence of the inexpensive nature of this amalgamation technique, ease to use and quite efficient gold recovery, it is the method of choice for current small-scale gold mining (SSM) nations in the developing world. The socio-economic merits of gold production by this methodology for the both past and present are obvious today; nevertheless, gold mining with mercury (Hg) faces strong opposition by the international community. This is primarily due to the toxicity of alkyl-Hg compounds, namely methyl-Hg (MeHg), which bio-accumulates and result in deleterious effects on humans and ecosystem functions. MeHg in fish has been linked to neurological damage popularly known as “Minamata disease” and myocardial infarction (D'Itri and D'Itri, 1977; Harris et al., 2003). Past Hg incidents are the disaster in

Minamata, Japan in the 1950s (Klein and Goldberg, 1970; D'Itri and D'Itri, 1977) and food poisoning reported in Iraq, Pakistan, Ghana and Guatemala (Bakir et al., 1973; Derban, 1974; Zhrlich, 1990), which resulted in numerous deaths. Following these fatal incidents, developed countries outlawed and phased out use of Hg in both mining and several non-mining industrial activities. Nevertheless since the advent of the new gold rush in the 1980s, as a result of socio-economic predicaments common to most developing nations, use of Hg to mine gold has rebounded and increased in spite of inception of cyanidation technology. The case of the tropical developing nations is an ongoing situation (Porcella et al., 1997; Bonzongo et al., 2004). Overall, the small-scale gold mining (SSM) industry around the world remains an important source of Hg introduction into natural systems by human activities, and Hg released to the environment from gold mining alone averages 450 tons/year; representing about 10% of the global anthropogenic Hg emissions (Larceda, 1997, 2003).

This study investigates the impact of gold mining on Hg biogeochemistry and cycling in a tropical aquatic system, the Pra River and its major tributaries, in southwestern Ghana, West Africa. In this region, changes in hydrology are driven by wet and dry cycles that affect the biogeochemistry of Hg introduced into the aquatic systems by artisanal gold mining. It is hypothesized that: (1) during rainy period soils become saturated with water leading to the production of methyl-Hg from Hg contaminated soil sources, which is then transported into the river channel via run-offs; (2) The Pra River Basin sediments have the potential to produce/degrade methyl-Hg; and (3) solar radiation could play a significant role in the production of methyl-Hg.

This dissertation includes: (i) a review of the literature emphasizing the history and environmental impacts of the use of Hg in gold extraction; (ii) data on both levels and speciation of Hg in different environmental compartments of the river system studied; (iii) the calculated potential rates of Hg transformation in soils/sediments and the likelihood for its bioaccumulation; and (iv) a preliminary assessment of the role of solar radiation on Hg cycling in tropical water bodies draining heavily vegetated watersheds.

.....they program various combinations of known facts about the present world and read out from computers' analyses the social and ecological consequences of various courses of actions. But, in fact, the real future is likely to be different from any of the predictable futures.

-René Dubos. *A God Within*



## CHAPTER 2 GOLD MINING AND MERCURY POLLUTION

### 2.1 Introduction

Mercury (Hg) pollution is a significant environmental issue because of its toxicity to organisms. Bioaccumulation of Hg in the muscle tissue of fish has become an increasingly problematic issue throughout the world and poses a health hazard for humans in many localities. Thus, growing public awareness of the dangers associated with the release of this toxic chemical has created demands for information on both background levels in the environment and the degree to which Hg could be concentrated in the food chain. This concern is gravely reflected in innumerable publications from international conferences as well as scientific literature on Hg as an environmental pollutant.

Severe troubles with methylmercury (MeHg) poisoning dates back to the 1860s in England, where synthesis of such mecurials was carried out. Subsequently, other cases arose through occupational and dietary exposures (Clarkson et al., 2003). Nevertheless, low level Hg toxicity to humans was not noted until the late 1950s. The industrial discharges of Hg into Minamata Bay and the Agano River in Japan resulted in accumulation of the toxicant in fish. The consequences were several mass poisonings, which attracted the attention of the scientific community. The inhabitants in fishing communities along Minamata Bay suffered an epidemic of neurological disorders, visual constriction, brain damage and eventual paralysis, which in numerous cases resulted in coma or death; afterward these were attributed to Hg poisoning from fish consumption

from the bay (Klein and Goldberg, 1970; D'Itri and D'Itri, 1977). Other incidents of Hg outbreaks were reported in Iraq, Pakistan, Ghana and Guatemala, with numerous deaths resulting from eating Hg-contaminated fish or consumption of foods prepared from seed grain treated with mercurial fungicides (Bakir et al., 1973; Derban, 1974; Zhrlich, 1990).

Hg cycles in the environment as a result of natural and human activities. In the last three decades, there have been increased Hg discharges into the environment from anthropogenic activities. This has heightened concern for health problems that result from Hg contamination by international health organizations (e. g. World Health Organization- WHO) and other environmental pressure groups around the world. Previously global Hg emission to the atmosphere was blamed primarily on industrial and combustion sources from Europe and North America (Nriagu and Pacyan, 1988; Pirrone et al., 1996). Notwithstanding, the mining sector remains an important anthropogenic source of Hg emissions (Nriagu and Pacyan, 1988; Larceda, 1997; Villas Boas et al., 2001). The greatest concern is point source inputs from past and present mining activities that enter the environment through volatilization and direct inputs to soils and water bodies. Ultimately, volatilized Hg returns to the terrestrial environments through wet and dry deposition, a prime concern in many areas, the world over. In recent times small-scale gold mining (SSM) or artisanal gold mining (AGM) with Hg has been recognized as one of the main Hg pollution contributors from the mining sector. Previously it was considered insignificant to the global Hg cycle (Nriagu, 1979). For about three decades, this traditional, primitive and obnoxious process of amalgamation has been very popular in tropical countries (Pfeiffer et al. 1989). In the case of developed nations (e.g. USA and Canada), gold mining with Hg was abandoned and replaced by cyanidation technique

recognizing Hg as toxicogenic (Porcella et al., 1997; Larceda and Salmons, 1998).

Earlier, historic mining sites in Europe, North America and elsewhere applied this amalgamation technology because of its proven efficiency in gold recovery (Marsden and House, 1992; Nriagu, 1994; Nriagu and Wong, 1997). Therefore, the present burden of Hg pollution associated with the gold rush in the tropical nations is a depiction of an old tragedy (Nriagu, 1994).

Unfortunately, today, as a consequence of socio-economic predicaments in many developing nations in Africa, Asia, and Latin America, use of Hg to mine gold has rebounded and heightened in spite of the introduction of the conventional cyanidation technology and lately bacteria oxidation process currently in use in Ghana, South Africa and USA (Veiga et al., 1997; Larceda and Salmons, 1998). Resurgence of the gold rush in the 1970s and 1980s in many of these nations resulted in millions of people becoming partakers of this type of mining because of increasing poverty, the effects of natural disasters (as observed in Africa) particularly droughts, lack of alternative employment, climate change and its impact on crop production, “get-rich-quick” mentality and above all, to escape complete social marginalization (United Nations, 1996; Hangi, 1996; Veiga et al., 1997; Larceda and Salmons, 1998; ILO, 1999). This informal mining supplied miners with quick income; and though labor intensive, provided an answer to under-employment. In addition, it reduced rural to urban migration by providing work to rural people who would have left had this alternative not existed (Davidson, 1993; United Nations, 1996). Moreover, these miners affirm Hg amalgamation to separate fine gold particles from alluvial gold ores and soil to be an inexpensive, reliable, easy and highly effective process. Only simple tools are needed, it can be set up anywhere and absolves

miners from any capital investment for equipment (Nriagu and Wong, 1997; Larcada and Salmons, 1998) compared with the past mining that grew from individual rudimentary mining into more cooperative and capital intensive, use of heavy machinery on a large scale. In the environment, metallic Hg is oxidized and ultimately transformed into highly toxic MeHg by biotic and abiotic pathways. Eventually, MeHg species accumulates strongly in aquatic biota, resulting in its bio-magnification through different trophic levels. In this regard, numerous studies on Hg's biogeochemical cycling in the temperate environment have established its toxicity and hazardous nature. The result is has been implementation of various environmental regulations and policies. Contrastingly, in the tropical environment, not much has been achieved in terms of Hg research considering the complex and diverse nature of the tropical ecosystems. The only well-studied region in the tropics is the Brazilian Amazon (e.g. Martinelli et al., 1988; Malm, 1990; Pfeiffer et al., 1991; Reuther, 1994; Lacerda and Salmons, 1998; Villas Boas et al., 2001), and few studies in Asia and East Africa (e.g. Ikingura and Akagi 1996; Ikingura et al. 1997; Lin et al., 1997; Appleton et al. 1999; van Straaten 2000a, b; Kambey et al. 2001; Babut et al. 2001; 2003; Ogola et al., 2002; Adimado and Baah 2002; Maponga and Ngorima, 2003; Bonzongo et al., 2003, 2004; Campbell et al. 2003; Limbong et al., 2003; Dai et al., 2003), which demonstrate high variability with regard to biological diversity, bedrock geology, and biogeochemistry. Further, research on Hg cycling in tropical environments is still in its infancy (Burger, 1997; Miller and Lechler, 1998). Thus, tropical ecosystems are complex with specialized predators, species diversity, food web lengths, productivity and soil laterization and might respond differently to Hg contamination than temperate and boreal ecosystems. In this chapter, a review of past and present gold mining by Hg

amalgamation techniques and the resulting environmental impact is presented based on citations from North and South America, Europe, Asia, Africa, Australia and New Zealand.

### **2.1.1 Brief History of Gold Mining and Mercury**

Gold has been known since antiquity as lustrous yellow dense, soft, ductile and inert in air, thus resisting corrosion (Wise, 1966). Gold, also called Chrysos by the Greeks, appears to be the first metal used by man (Müezzinoğlu, 2003). It is a highly valuable metal and much sought after in ancient times. In addition, it is a symbol of prosperity, wealth, and above all, an asset since the Bronze Age (Müezzinoğlu, 2003). Even today, gold as described by Craig and Rimstidt (1998) is one of the most influential mineral commodities in human history and continues to be an object of great human desire. Because of its luster and durability, gold was used in ornamentation and coinage. Ultimately, it became the accepted financial basis of many societies. Chinese used gold in the form of flakes or dust as medicinal agent as early as 2500 BC. The Egyptians also applied gold to decorate their statues, tombs, crypts and sarcophagi in addition to employing it in cosmetics as direct adornment of their own bodies (Cohn et al., 1981; Craig and Rimstidt, 1998; Merchant, 1998). It is believed that gold had been mined, collected from alluvial and separated from the ores of silver, copper and other metals since prehistoric times (Merchant, 1998). Moreover, gold was recovered by swirling a mixture of auriferous sand and water in a shallow pan or separated using sluice box fitted with transverse riffles that retain the gold. Later recoveries were improved by adding a little Hg to the system, which tends to wet the gold particles and bind them together (Wise, 1966; Cohn et al., 1981).

On the other hand, metallic Hg and cinnabar have been known in the distant past (Drake, 1981). Among all metals, Hg has been extensively used by man since the advent of civilization. Until now, Hg is still being used in medications, industry, and agriculture. Yet Hg is also one of the most pernicious toxic chemicals ever known (Chang, 1997; Clarkson, 1997). The first documented report of Hg was by Aristotle in the 4<sup>th</sup> century BC, when it was used in religious ceremonies. Before then, cinnabar (also called vermillion) was used as pigment for cave and body decoration. The Egyptians, Greeks, and Romans applied Hg in cosmetic and medicinal preparations and for amalgamation (Drake, 1981; Müezzinoğlu, 2003). Later, in 1554, New Spain (now Mexico) developed the Patio amalgamation process into the industrial scale for the recovery of gold and silver, resulting in increased consumption of Hg (Drake, 1981; Nriagu, 1993). Equally, use of Hg in amalgamation dates back to the Phoenicians and Carthaginians as early as 2700 BC who discovered that the precious metal could be easily recovered on heating. Though there is a claim that the first application of amalgamation dates back to mining in Bosnia under the Emperor Nero (56-68 A.D.) (D'Itri and D'Itri, 1977; Hentschel and Priester, 1992). Notwithstanding, this technology had a widespread application only among the Romans around 50 A.D. Up to today, small-scale miners continue to use this technique intensively and unrestrictedly.

The Romans are believed to have imported 5000 kg/year of Hg from Spain to Italy solely for gold amalgamation. Environmental problems with the use of Hg in gold mining led the Romans to prohibit this activity in Italy after less than 100 years (D'Itri and D'Itri, 1977). Further, the fall of the Roman Empire also gave birth to diminished mining activity until its revival in the 11<sup>th</sup> Century in Central Europe. All gold mining activities

were concentrated around the Harz Mountains in Germany. Amalgamation and retorting processes were applied in gold extraction in AD 1400. Gold was also produced by the amalgamation technique using copper plates from areas of European exploration, such as West Africa between 1400 and 1600 (Marsden and House, 1992). In the Americas, use of Hg was launched in the 16<sup>th</sup> century by the Spanish to amalgamate silver and gold in Mexico, Peru and Bolivia applying the “Patio” process known for its efficiency at refining great volumes of inferior grade ore. This process consisted of spreading silver and gold powdered ore over large, paved flat surfaces and mixing it with salt brine and a mixture of Cu and Fe pyrites and elemental Hg (Nriagu, 1994; Nriagu and Wong, 1997; Larceda, 1997). This methodology, subsequently employed in South America, is said to have originated from European metallurgical practices after the sudden end of gold and silver mining in the 1550s (Marsden and House, 1992). All Hg employed in Spanish America came from Almaden (Spain), Peru, and Idria in modern Slovenia (Nriagu, 1993). From 1560 to 1700, over 20,000 tons of Hg was used by Mexican mines while Hg consumption in Peru reached over 50,000 tons in the same period (Larceda and Salmons, 1998). The application of “Patio” continued undisputed through the end of the 19<sup>th</sup> century. In spite of its convenience, it also led to discharge of unprecedented amounts of Hg to the American environment.

### **2.1.2 Gold Rushes Around the World**

In the 19<sup>th</sup> century, North America, New Zealand and Australia experienced a “gold rush” with its accompanying Hg problems. In 1799, gold mining commenced in the USA from exploitation of huge deposits in North Carolina streambeds to be quickly followed by the Appalachian gold rush reaching as far as south Alabama. These rushes were much smaller than later ones in the West in the 1800s. This subsequent gold discovery led to

unparallel movement of people and increased population in many of these regions; typical examples were California, South Dakota and Alaska gold rushes. Gold was primarily concentrated using Hg amalgamation in California, Colorado, Georgia, Alabama, Nevada, South Dakota and other states during the gold rush, and later in Klondike, Yukon-Canada in 1896-1901 (Marsden and House, 1992; Nriagu, 1994; Nriagu and Wong, 1997; Da Rosa and Lyons, 1997; Wong et al., 1999; Craig and Rimstidt, 1998; Brands, 2002). In many instances slave labor was used.

Similarly, the Australian gold rush commenced in 1851 at Bathurst (New South Wales), Ballarat and Bendigo in Victoria. More gold was discovered in New South Wales, Queensland, Western Australia and New Zealand subsequently (Manten, 1968; Bycroft et al., 1982; Marsden and House, 1992; Nriagu, 1994; Nriagu and Wong, 1997; Churchill et al., 2004). Like the USA and Canada, these nations also depended principally on gravity concentration and Hg amalgamation as the main extraction technique for gold. On the other hand, Russia in the first half of the 19<sup>th</sup> Century was the major producer of gold in the world. Gold was mined in 1774 near Ekaterinburg. Later, the discovery of gold in Siberia in 1838 on the Ulderey River resulted in a gold rush that was restricted only to the local population. Significant mining also took place in the Lena Basin from 1846. Higher Hg concentrations in the environment were associated with the Hg amalgamation process (Marsden and House, 1992; Nriagu and Wong, 1997; Laperdina, 2002). According to Yagolintser et al. (1996), Siberian gold production accounted for more than 20% of anthropogenic Hg emissions. Vasiliev et al. (1998) also pointed out that after World War II amalgamation was widely applied in most gold extracting plants of USSR. At present, Hg amalgamation in Russia is practiced only for



small-scale placer gold mining. In addition, illegal and uncontrolled use of Hg in gold mining still persists to today (Laperdina et al., 1995a, 1996b; Yagolintser et al., 1996; Vasiliev et al., 1998; Laperdina, 2002). Lastly, South Africa also experienced a gold rush between 1873 and 1886 following discovery of gold in Lydenburg, Witwatersrand and other localities. In like manner, Hg amalgamation was the method of mining (Rendall and Van Sittert, 1984; Marsden and House, 1992; Nriagu and Wong, 1997).

In developing nations, gold mining by Hg amalgamation remains the method of choice (Pfeiffer and Larceda, 1988; Pfeiffer et al., 1993; Greer, 1993; James, 1994; Ikingura et al., 1996; Lin et al., 1997; Larceda, 1997; Larceda and Salmon, 1998; Miller and Lechler, 1998; Dai et al., 2003; Aryee et al., 2003; Maponga and Ngorima, 2003; Maponga and Ngorima, 2003; Ogola et al., 2003; Bonzongo et al., 2003; 2004). This occurred primarily in South and Central America, Africa, Asia, and to some extent in Russia. As noted elsewhere, gold has been one of the most powerful stimuli, as well as important revenue in the economy, of many developing tropical nations as it prevailed in the past developed temperate nations. Hence, it is no surprise in the present gold rush that Brazil is first in South America and second in the world in gold production, with 90% of this coming from SSM or informal mining. All the same, there are few small placer miners (group or individual prospectors) also using Hg in Australia, USA and Canada (Leigh, 1997; Donoghue, 1998; Larceda, 1997; Larceda and Salmons, 1998; Malm, 1998; Meech et al., 1998; Larceda, 2003). Today in many of the developing countries, SSM is the largest single source of Hg emissions. It is believed that Hg from SSM to the environment may reach an input of about 450 tons of Hg annually, mostly from South

America and Asia, and may account for 10% of overall total anthropogenic flux of Hg into the global environment (Porcella et al., 1997; Larceda, 1997; Larceda, 2003).

## **2.2 Gold Mining Processes and Amalgamation Technology**

The Hg amalgamation technique used in past gold mining activities differs little from the present day amalgamation technique used in the developing nations. In the past, a variation of the Patio amalgamation process was used in North America. The processing of the gold or silver ores involved extraction of ores deposits from placer deposits (alluvial) or deep shaft mines and their shipment to stamp mills where they were pulverized and mixed with water, various salts and Hg to produce gold/silver amalgam. By distillation of the amalgam, Hg was condensed for recycling, and the pure metal was recovered, which is not a popular practice with present gold miners. Thus, most of the Hg used could be retrieved, yet substantial quantities were lost with the discarded milled fine tailings to the environment during every stage in the amalgamation process due to low technology and working conditions (Nriagu, 1993, 1994; Nriagu and Wong, 1997; Miller and Lechler, 2003). In addition, panning, being cheap and easy to use method was always utilized in prospecting placer deposits. Auriferous sand was swirled with water in pan to concentrate the denser gold particles before amalgamation. The amalgam was then squeezed through a buckskin bag and excess Hg recycled into a barrel. The bag was then retorted or heated on a shovel to remove Hg (Nriagu, 1994; Nriagu and Wong, 1997; Da Rosa and Lyons, 1997; Craig and Rimstidt, 1998). On a large scale, sluicing was employed in conjunction with other procedures in the recovery of gold in North America, Australia and New Zealand. Sluicing involved pouring the ground ore from river beds or hard rocks into a sluice, a long trough that contains a series of upraised riffles made of Hg-coated copper plates to which the gold particles adhere. The denser gold particles

were trapped in the bottom by the riffles, while the less-dense ore was washed away.

Excess Hg was removed from the cleaned amalgam by squeezing through a strong cotton cloth. Pure gold was obtained after subjection to heating or retorting and melted in oil-fired furnace as done in Nova Scotia, Canada (Henderson, 1935; Manten, 1968; Nriagu and Wong, 1997; Da Rosa and Lyons, 1997; Craig and Rimstidt, 1998; Donoghue, 1998).

In 1853, hydraulic mining was introduced in California and subsequently in both eastern and western states of USA and in 1900 in Yukon Canada. In this case, mining involved spraying high pressure streams of water against river gravel banks, canyons or channels and capturing run-off in long sluice boxes often equipped with Hg to trap the finer gold particles as described earlier. Many rivers were dammed to ensure water supply for the various mining sites. This escalated the rate at which placer deposits could be exploited. Nonetheless, this methodology of mining came under severe restriction because of its destructive effects on rivers and bays, since hydraulic mining for gold mobilized sediments and choked natural streambeds spreading Hg contamination. In addition, it deposited a lot of mine wastes in many areas affecting agriculture. Hg amalgamation was also used on dredged gold-bearing sediments (Nriagu and Wong, 1997; Da Rosa and Lyons, 1997; Craig and Rimstidt, 1998; Alpers and Hunerlach, 2000).

On the contrary, in the developing world, operations of AGM activity are almost the same, apart from a few differences that may be site specific. Figure 2-1 shows a general example of gold extraction methodology common to all mining sites. It is generally accepted that present mining operations in the tropical regions and elsewhere are small scale and inefficient compared with past historic large-scale mining sites (Miller and Lechler, 1998). Most authors point out that, in contrast to the historic mining

sites in temperate regions, gold mining by amalgamation in the tropics are spearheaded by two principal procedures employing rudimentary equipments, instead of heavy machinery. The initial process involves extraction of gold from alluvial soils and rock (most at times underground), and is practiced in all the tropical countries in Africa and South America, as well as some parts of Australia, Eastern Europe and Asia. This consists of excavating large amounts of gold-bearing material usually from surface soils/rocks containing quartz veins or alluvial deposits using rudimentary tools (e.g. shovels, pick-axes, and chisels), which are ground in locally fabricated ball mills or locally designed metal or wooden mortars and pestles that are very common with African, Brazilian and Chinese miners. This is followed by gravity separation involving simple panning or washing of powdered ore on short inclined sluiced boxes shaped like stairs to produce gold-rich concentrate, which is later, amalgamated with Hg. In some cases, the bottom of the sluice is lined with cloth, which is continuously impregnated with Hg similar to the past to make the fine and heavy metallic particles of the gravel

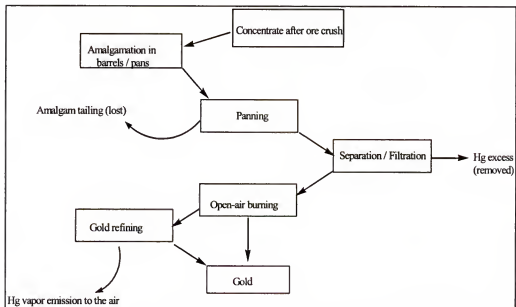


Figure 2-1. Typical amalgamation process in gold mining nations.

agglutinate in the cloth. The washing is manual and consists of pressing the gravel against the cloth. Large amounts of Hg are used to prevent water from washing away gold particles. Non-biodegradable powdered soap is sometimes put in the riffle to diminish the Hg capacity of flooring, thereby making Hg float. This enhances adherence of gold particles on entering the riffles that was not the case with historic mining. The minimum amount of Hg used at mining sites in most nations is about 2-4 kg of Hg per kilo of gold produced. Sometimes others use as much as 10 kg of Hg to 1 kg of gold typical with Brazilian Amazon and African miners. However, usually about two-thirds are consumed in the amalgamation process in the riffles. The remainder eventually ends up in the rivers or ponds as observed in the earlier mining (Mallas and Benedicto, 1986; Pfeiffer et al., 1993; Salmons, 1995; Ikingura et al., 1996; Larceda, 1997; Lin et al., 1997; Babut et al., 2003; Maponga and Ngorima, 2003; Aryee et al., 2003; Nriagu and Wong, 1997; Da Rosa and Lyons, 1997; Alpers and Hunerlach, 2000). In the case of China, often amalgamation is followed by flotation of tailings (Lin et al., 1997; Gunson and Jian, 2001). Like the historic mining sites, the separated amalgam is ultimately obtained by pressing it through a leather, cloth or aluminum foil and burned with gas torch or in retorts. In Africa, Asia and the Brazilian Amazon, some miners use bonfire, charcoal fire, or open crucible as is the case of Indonesia and the Philippines. Additionally, in Indonesia, normally sodium borate (borax) is added to the burning amalgam as a cleansing agent to remove any impurity from the pure gold (Limbong et al., 2003) whereas in Latin America and Africa (e.g. Venezuela and Ghana), dilute nitric acid or aqua regia is used for the same purpose for decomposition of the amalgam (Amegbey et al., 1997; Veiga, 1997; Hentschel and Priester, 1992), similar to practices reported for

Goldenville miners in Canada (Henderson, 1935). Unlike the historic sites, these miners do the roasting in the local towns, in huts along the rivers or in their residence, thus dispersing Hg into the atmosphere. Others (e.g. Brazil, Ghana and Tanzania) also perform this operation in open air with miners inhaling fumes of Hg gas. Losses to the environment also occur as a consequence of poor handling and volatilization during processing as observed in the past gold mining in temperate regions (Pfeiffer et al., 1993; Salmons, 1995; Ikingura et al., 1996; Larceda, 1997; Larceda and Salomons, 1998; Maponga and Ngorima, 2003; Babut et al., 2003; Aryee et al., 2003). Furthermore, sponge gold containing about 20g of Hg per kg of gold is liberated at the gold shops when melted. Studies show that most of this Hg is deposited near the emission source (Veiga, 1997). In short, most Hg is lost during the stamping, grinding, separation of amalgam, retorting and refining of gold and silver bullion. However, losses were exceptional at the historic sites because other salts were added to aid smooth amalgamation that resulted in most instances in the formation of insoluble Hg compounds (Nriagu, 1994; Nriagu and Wong, 1997). Currently, tropical countries and some parts of Australia and Russia also follow the same rudimentary techniques (Laperdina et al., 1995a, 1996b; Lin et al., 1997; Donoghue, 1998; Gunson and Jian, 2001; Laperdina, 2002). Meanwhile, amalgamation tailings are left behind to form Hg “hot spots” (Larceda et al., 1991; Kehrig et al., 1997; Veiga, 1997; Meech et al., 1998; Larceda and Salmons, 1998).

In the second approach, gold is extracted from bottom sediments normally dredged from the river beds. This was greatly practiced at historic sites. Now this is very common in Amazonian basin and some parts of Asia and Africa (Ghose, 1994; Salomons, 1995;

Larceda et al., 1995; Kligerman et al., 2001) and today is still utilized in some areas in Australia (Donoghue, 1998) and Russia (Laperdina et al., 1995, 1996; Laperdina, 2002) together with hydraulic mining. The gold-ore after process is separated by amalgamation and roasted.

### **2.2.1 Mercury Discharges to the Environment due to Past and Present Gold Mining Activities**

In temperate regions, gold has played a significant role in the settlement and economics of North America. In the USA, commercial production from 24 states totaled more than 420 million troy ounces (13,000 metric tons) from 1804 through 1995 (Craig and Rimstidt, 1998). It is believed that 60,000 tons of Hg were released into the environment from the United States gold rush, and 196,000 tons were distributed in both South and Central America (Nriagu, 1994), most of which are still trapped in mine tailings/soils and sediments (Nriagu, 1994; Callahan et al., 1994; Bonzongo et al., 1996; Mastrine et al. 1999). This is evident in the elevated Hg contents of various environmental compartments and fish downstream of historic mining sites. Droplets of metallic Hg and gold grain partially coated with Hg were recovered from soil in mining trenches and sediment measuring up to 7.4 ppm (Callahan et al., 1994) in North Carolina mining sites. Smith (1943) also estimated that 6800 tons of Hg was lost during the mining of the Comstock Lode of the Carson River basin; whereas Mastrine et al (1999) reported 15-32 tons of Hg was discharged into the Dahlenega Mining District environment by 1900. The amount of Hg lost to the environment from lode gold mills in California is estimated to be about 2000 tons (Churchill, 1999). Presently, it is well known that many of these mining operations that were initiated in the 19th century have become today's hazardous waste Superfund sites. A good example of superfund site is the Clark Fork

River basin, near Butte, Montana, where extensive destruction was caused by tailings discharged into rivers and streams (Da Rosa and Lyons, 1997).

In Canada, in Goldenville-Nova Scotia alone, where mining lasted from 1860 to 1940, production of 6.24 tons of gold (Wong et al., 1999) left  $3 \times 10^6$  tons of tailings containing as much as 6.8 tons of Hg. Records also show that amalgamation technique was used in all the gold bearing regions in Canada until the 1978. In all, 500 mills throughout the country practiced amalgamation with 150 operating in Ontario (Trip et al., 2004), releasing even more Hg to the immediate environment (Nriagu and Wong, 1997). Gaudet et al. (1995) documented that, in Canada anthropogenic release of Hg to the environment has been approximately 31 tons annually. It is also estimated that over 4540 tons of Hg were used in the Alaskan and Klondike goldfields. In general, in both Canada and USA, as much as  $1.5 \times 10^{-3}$  tons of Hg were lost for every kg of precious metal produced. Hg loss of about 0.3 to 3.0 kg/ton of ore processed was observed in western USA mills (Nriagu and Wong, 1997).

In Australia, up to 900 tons of Hg were estimated to have been lost to the environment in Bendigo field of Victoria between 1850 and 1930, with significant levels accommodated in the tailings. The weight of Hg used was similar to the weight of gold recovered in the amalgamation process (Bycroft et al., 1982). Until 1916 in Wales, the amalgamation technique was applied in gold mining and is believed to have resulted in Hg contamination of Mawddach River (Fuge et al., 1992). Similarly, in the gold rush in New Zealand, about the same period as that of California and Australia, the Hg-amalgamation process was practiced and lasted into the twentieth century (Manten, 1968; Donoghue, 1998) leaving an unbelievable Hg legacy in the environment. In Russia, it is



accepted that maximum consumption of Hg eventuated when sluiced amalgamation was practiced on dredge and Hg up to 0.42 tons was applied on the rugs of sluices. Hg losses were estimated to be 55-70 mg m<sup>-3</sup>; and 34-80 tons/year Hg emissions have been estimated for the former Soviet Union. The Hg content in dredged tailings could reach 0.2g m<sup>-3</sup> as a result of mechanical losses. Before 1988 the total irreversible losses of Hg by amalgamation of gold on dredges could peak at 6 tons/year and at gold dressing plants about 3 tons/year. Accordingly, there is a large amount of tailings containing not only Hg, but also arsenic, zinc, copper, silver, lead, chromium, cadmium, sulfide minerals and iron pyrite that could generate acid mine drainage. Though currently Hg amalgamation is outlawed, limited uncontrolled use of Hg in some areas does continue (Laperdina et al., 1995a, 1996b; Yagolinitzer et al., 1998; Vasiliev et al., 1998; Laperdina, 2002).

Correspondingly, in the tropics presently, the quantity of Hg used to extract gold is approximately the same as the quantity of gold retrieved (Pfeiffer et al. 1988, 1989, 1993; Larceda and Salomons, 1998; Korte and Coulston, 1998; Babut et al., 2003). In other places, more than 1:1 is applied in the extraction procedure as observed in tropical Africa and South American countries (Pfeiffer et al. 1989, 1993; Hangi, 1996; Larceda and Salomons, 1998; Bidone et al., 1997a, b; Babut et al., 2003). Thus, in Brazil, by the ratio of 1:1, it implies about 100 tons of Hg are lost yearly. In most Amazonian countries nearly double this quantity of Hg is dispersed annually. Barbosa et al (1995) presumed that about 2000 tons of Hg might have been emitted into the environment since the advent of the new gold rush in the 1980s. Pfeiffer et al. (1989) also claimed that the current loss accompanying gold extraction in the Amazon, about  $(1.3-1.7) \times 10^{-3}$  tons per  $10^{-3}$  ton of gold recovered, based on the rule of thumb in Potosi (now Bolivia) that 1.5 x

$10^{-3}$  tons of Hg lost for  $10^{-3}$  tons of silver produced (Nriagu, 1994), is closer in magnitude to Hg discharges from colonial silver mines after the 18<sup>th</sup> century. Consequently, since the beginning of the new gold upswing in developing countries at the end of the 1970s, it is believed that about 5000 tons of Hg has been discharged into the South American environment (Valenzuela and Fytas, 2002). Although accurate estimates are hard to obtain (Table 2-1), Malm (1998) indicates that about 240 tons of Hg is released into the environment annually from mining operations in the Brazilian Amazon, Venezuela, Colombia, and Bolivia. A portion of this Hg is lost to the atmosphere during the burning of the amalgam, and the remaining enters rivers and lakes (Pfeiffer and Larceda, 1988; Pfeiffer et al., 1993). Nriagu and Wong (1997) indicated that Hg lost at historic sites in USA was about 1360 tons/year from 1850 to 1900 and far outweighed input in the Brazilian Amazon associated with current gold rush. These authors believed that Hg losses were higher in the historic period because of poor technology and carelessness on the part of miners than the present losses in the new gold rush in the tropics. Even with advanced technological innovations, the loss of Hg in the mills of western USA remained high and generally varied from 0.3-3.0 kg/ton of ore processed (Nriagu, 1994; Nriagu and Wong, 1997). Pirrone et al. (1996a, 1998b) reported that Hg released during pre-industrial times in gold and silver recovery are much higher than that released presently. Table 2-1 illustrates the point. The numbers are mostly from South America. Estimates from Africa, Asia and Eastern Europe continents are conspicuously absent except for the

Table 2-1. Estimated Mercury Input to the Environment Due to Gold and Silver Mining

	Period	Total Input (tons)	Annual input (tons per year)
Spanish Colonial America	1554-1880	196,000	600
All North America	1840-1900	60,000	1000
Colonial Brazil	1800-1880	400	5
Brazilian Amazon	1979-1994	2,300	150
Venezuela	1988-1997	360	40
Columbia	1987-1997	240	30
Bolivia (Pando Department)	1979-1997	300	20
Philippines	1985-1997	200	26
Tanzania	1991-1997	24	6
China	1992-1997	480	120

Source: Malm, 1998

case studies reported for Philippines, Tanzania and China, Table 2-1. A recent inventory reported for Tanzania and Zimbabwe put Hg emission at about 11 tons/year (Ikingura et al., 1996, 1997; Straaten, 2000a, b; Larceda, 2003), whereas in the Philippines, Hg discharges now vary from 15-47 tons/per year (Cramer, 1990; Appleton et al., 1999; James, 1994).

Therefore, there is the belief that old tailings in drainage basins are significant sources of Hg contamination to the local environment even after mining operations have ceased. As a result, in many historic gold mining areas, water, sediment and soil contamination from Hg remaining after several years of amalgamation have been noted in USA; for example, Carson River and Lahonton Reservoir, downstream of the Comstock Lode in Nevada (Hesse et al., 1975; Prokopovich, 1984; Callahan et al., 1994; Bonzongo et al., 1996; Lechler et al., 1997; Miller et al., 1998) and the Chestatee and Etowah River watersheds near the Dahlonega area in Georgia (Leigh, 1994, 1996). Likewise, in Nevada

and Quebec, parlous levels of Hg in fish are thought to have resulted from historic amalgamation plants, have been reported (McKeown-Eyssen and Ruedy, 1983; James, 1994; Gustin et al., 1994). More so, lakes in many parts of the Yukon, Canada, contain fish with unimaginable levels of Hg, and the body burdens of Hg in many native Canadians are above the threshold of health concern (Wheatly and Paradis, 1995; Nriagu and Wong, 1997); and Hg as much as 500 mg/g in mine tailings is still present in Nova Scotia (Larceda and Salmons, 1998). In regions of Russia, Hg contamination of soils ( $18.9 \text{ mg Kg}^{-1}$ ), ground water ( $3280 \mu\text{g L}^{-1}$ ) and bottom sediments ( $52.2 \text{ mg Kg}^{-1}$ ) have been documented (Laperdina, 2002); and in Siberia-Russia, Hg assimilation by plants has been noted (James, 1994). In Australia and New Zealand, Hg contamination of waterways, land and biota due to gold mining by Hg amalgamation process are well described (Bycroft et al., 1982; Craw and Chappell, 2000; Redmayne et al., 2000; Churchill et al., 2004).

Accordingly, studies in the Brazilian Amazon with some supplementary research in Africa and Asia have confirmed environmental contamination of ecosystems as a result of Hg releases from AGM. Numerous reports on past gold mining sites in developed nations show the persistence of Hg as an environmental pollutant. From these reports, it is obvious that Hg pollution left behind during the first gold rushes remains evident and is a continuing hazard to the people and wildlife of the impacted regions. In the case of current gold mining nations, the weight of the implications is yet to “haunt” them.

In view of this, there has been an extraordinary Hg emission control in most developed nations leading to a substantial fall in global Hg inputs into the environment unlike the gold-rich developing nations where mining of gold by amalgamation is on the

increase. As observed by Nriagu (1990) Hg emissions fell to 6000-13,500 tons/year in the late 1980s and are believed to be the effectiveness and stringent Hg control policies and the emergence of the cyanidation technique. In developing countries, the major setback common to all is probably the lack of financial support for scientific research; ineffective environmental protection agencies to enforce compliance of environmental policy and regulations, if they exist, and the limited number of large scale industrial activities that would raise concern about environmental quality (Bonzongo et al., 2004). Ghana, the focus of this study, is not an exception.

## **2.3 Fate of Mercury Introduced into the Environment**

Artisanal gold mining releases metallic Hg ( $\text{Hg}^0$ ) directly to soil, water, and sediments during the amalgamation process and to the atmosphere during the torching of the obtained Au-Hg amalgam and later gold purification, which takes place in gold shops. In each of these environmental compartments,  $\text{Hg}^0$  undergoes transformations ultimately to produce chemical species that are readily bioavailable, leading to Hg bioaccumulation. The released Hg vapor to the atmosphere and its subsequent accumulation in foods lead to human exposure to Hg via inhalation and diet. Figure 2-2 summarizes the pathways by which  $\text{Hg}^0$  is released as a result of gold mining by Hg amalgamation in the environment; the aspects of the biogeochemical cycling of Hg are presented below.

### **2.3.1 Gold Mining and Atmospheric Pollution with Mercury**

The fate of  $\text{Hg}^0$  released to the atmosphere during the different steps of gold extraction/purification is rather complex and influenced by climatic factors. As indicated in section 2.2 (see Figure 2-1), the obtained gold rich concentrate from crude ores is usually mixed with  $\text{Hg}^0$  to form the Hg-Au amalgam, which is then filtered or squeezed

to remove excess water and Hg. In each of the amalgamation steps before retorting or roasting, Hg is lost through vaporization from drops left in pans/barrels, degassing from

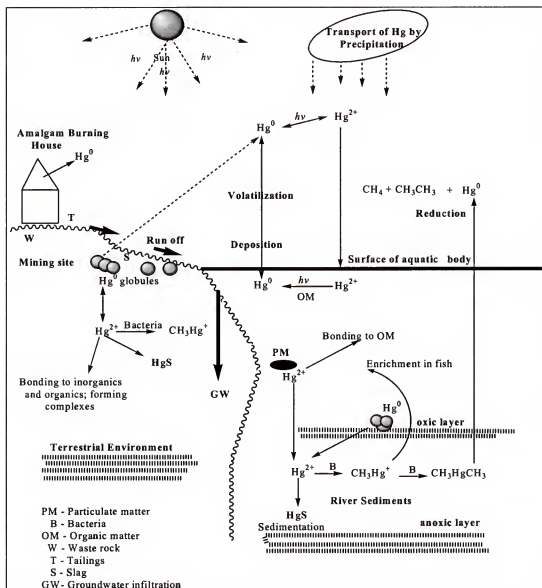
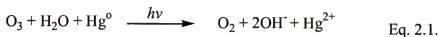


Figure 2-2. Main pathways for Hg released from AGM to the environment (adapted from Melamed and Villas Boas, 2000).

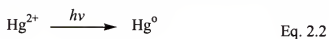
discarded milled fine tailings or as a result of poor handling of the chemical during storage, transport and charging into mills, barrels or pans. Retorting of the amalgam was done mostly in the past, whereas open burning of the amalgam is characteristics of current AGM in developing nations. This process results in the introduction of Hg vapor

directly into the atmosphere through volatilization, (Figure 2-2). In addition to  $\text{Hg}^0$ , other Hg-complexes such as  $\text{HgO}$  have been identified in the “flue gas” coming from the burning of Au-Hg amalgams (Lacerda and Salmons, 1998). Finally, the re-burning to retrieve gold bullion at the gold refinery shops, a practice common to both old and new mining sites, results in a significant atmospheric emission of Hg (Pfeiffer et al., 1993; Nriagu, 1994; Nriagu and Wong, 1997), Figure 2-2.

$\text{Hg}^0$  released to the atmosphere from the different Au-extraction stages can undergo atmospheric oxidation through reactions mediated by ozone, solar energy and water vapor to yield  $\text{Hg}^{2+}$  (Eq. 2.1). Particle reactive and soluble  $\text{Hg}^{2+}$ -compounds are



then returned to the terrestrial environments by wet/dry deposition (Lindqvist and Rhode, 1985; Ivertfeld and Lindqvist, 1986). Under the hot tropical atmospheric conditions,  $\text{Hg}^0$  oxidizes quicker than in temperate atmospheres (Hacon et al., 1995; Lacerda, 1995), and such oxidation is faster in the presence of ozone and soot emissions that come from forest burning (Hacon et al., 1995; Lacerda, 1995). As a consequence, and in comparison with temperate regions, shorter residence times in the atmosphere and higher atmospheric deposition rates of Hg have been reported for the Brazilian Amazon (Lacerda et al., 1999; Marins et al., 2000), limiting the long-range transport of Hg and contamination of distant ecosystems. Once deposited on soil and/or aquatic landscapes, further transformations occur including reduction of atmospherically deposited  $\text{Hg}^{2+}$ , catalyzed by biotic and/or abiotic processes, to  $\text{Hg}^0$  (Eq. 2.2) and the return to the atmosphere via volatilization (Figure 2-2). On a global scale, this cyclic behaviour sustains the flux of Hg between



the atmosphere and terrestrial landscapes (Nriagu, 1994; Nriagu and Wong, 1997; Larceda and Salomons, 1998).

The atmospheric portion of the Hg cycle is dominated by inorganic species, primarily  $\text{Hg}^0$ . Despite the presence of methyl-Hg in rain water samples (Rudd, 1995), there are no known chemical pathways for atmospheric methyl-Hg production. It is believed that terrestrial sources (e.g. wetlands, landfills) release alkyl-Hg (mono- and dimethyl Hg) compounds to the atmosphere (e.g. Lindberg et al. 2001 and 2005).

### **2.3.2 Gold Mining and Mercury Pollution of Terrestrial Landscapes**

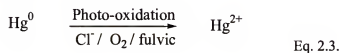
In the past, gold ore from placer deposits and deep shaft mines was pulverized at stamp mills before Hg amalgamation, while current gold miners depend mostly on ground gold rich soils and active bottom or river bank sediments (Pfeiffer et al., 1993; Nriagu and Wong, 1997). Therefore, in addition to Hg contamination of terrestrial landscapes via atmospheric deposition,  $\text{Hg}^0$  enters aquatic and terrestrial systems directly during the stamping, grinding, sluicing, panning, and amalgamation processes. Mine wastes rich in  $\text{Hg}^0$  are usually left on riverbank soils, concentrated in mining ponds, or directed to nearby waterways where they become dispersed through fluvial processes (Bonzongo et al., 2002). In AGM impacted sites, droplets of  $\text{Hg}^0$  are often found at roasting and amalgamation sites (Pfeiffer et al., 1989; Pfeiffer et al., 1993; Nriagu and Wong, 1997; Miller and Lechler, 2003). As stated earlier,  $\text{Hg}^0$ -contaminated terrestrial landscapes would then become a source of Hg to the atmosphere. On the other hand,  $\text{Hg}^0$  concentrated in tailings would be eventually mobilized through leaching, infiltration, surface run-offs, and particle transport into aquatic systems (Pfeiffer and Larceda, 1988; Pfeiffer et al., 1989; Nriagu et al., 1992; Wayne et al., 1996; Laperdina et al., 1995a,



1996b; Nriagu and Wong, 1997; Lin et al., 1997; Craig and Rimstidt, al., 1998; Veiga, 1997; Wong et al., 1999; Melamed and Villas Bôas, 2000; Laperdina, 2002). Hg leaching from soil is also accelerated by shifts in soil land use (Larceda, 2002). Overall, the above transport mechanisms lead to contamination of both surface and ground waters, and they are more pronounced in regions with high annual precipitation (Mudroch and Clair, 1986; Nriagu and Wong, 1997; Wong et al., 1999; Callahan et al., 1994).

In aquatic systems, the low solubility of  $\text{Hg}^0$  in water at ambient temperature leaves most of it subject to volatilization. However, recent reports on redox chemistry of Hg at the water-atmosphere interface show that solar radiation driven oxidation of  $\text{Hg}^0$  occurs at rates greater than that of the reduction of  $\text{Hg}^{2+}$  to  $\text{Hg}^0$  (e.g. Lalonde et al. 2001). The produced  $\text{Hg}^{2+}$  will tend to partition between the aqueous and solid phases, and due to its particle-reactive nature, Hg will predominantly accumulate in bottom sediments following the settling of Hg-contaminated particles. Sediments act as sinks for most pollutants including Hg. However, over time, sediments tend to behave also as a source by releasing Hg back to the water column as a result of physical (e.g. bio-turbation, diffusion), microbial and/or chemical processes (Kudo, 1992).

Besides the different transport pathways discussed above,  $\text{Hg}^0$  introduced in either soils or sediments can also be oxidized to  $\text{Hg}^{2+}$ . In fact, laboratory simulations have shown that, in solar exposed oxygenated environments and in the presence of species such as chlorides and organic acids (e.g. fulvic and humic),  $\text{Hg}^0$  is easily oxidized or photo-oxidized to  $\text{Hg}^{2+}$  (Eq. 2.3) (de Magalhaes and Tubino, 1995; Yamamoto et al., 1995; Yamamoto, 1996).



It is believed that this reaction could take place in wet surface soils and in surface sediments of littoral zones, producing the readily available  $\text{Hg}^{2+}$ .

The environmental Hg transformation of ecological importance is that of the conversion of inorganic Hg species to organo-Hg compounds, namely mono-methyl-Hg. If Hg released from gold mining is primarily in the inorganic form, Hg found in tissues of organisms inhabiting mining impacted system exists predominantly as methyl-Hg (Grieb et al., 1990; Bloom, 1992; Watras and Bloom, 1992; Kim, 1995). Thus, inorganic Hg entering aquatic systems must either be converted mostly to methyl-Hg prior to bioaccumulation (Gilmour and Henry, 1991) or methylated less so after its bioaccumulation. Either way, this points out the importance of understanding the processes responsible for methyl-Hg production as a primary step in understanding the bioaccumulation of Hg and the resulting Hg toxicity.

Non-biological as well as biotic processes may mediate environmental methylation of inorganic Hg. Although the relative contribution of these processes to the observed ambient MeHg levels has not been clearly defined (Gilmour et al., 1991; Weber 1993), experimental evidence suggests that microbial transformations play a key role in the biogeochemical cycling of Hg (Compeau and Bartha, 1985; Berman and Bartha, 1986; Barkay, 1992). Investigation of Hg transformation in anaerobic soils and sediments points to sulfate reducing bacteria (SRB) as key players in Hg methylation. In fact, soil or sediment samples spiked with inhibitors of bacterial sulfate reduction (i.e. molybdate, selenate, tellurate, and tungstate) showed a significant decrease or a total inhibition of MeHg production compared with un-amended samples, indicating that methylation by SRB was the important source of MeHg formation in the sediments (Compeau and

Bartha, 1985; Gilmour et al., 1992; Bonzongo et al., 1996; Chen et al., 1997). These studies also showed that addition of sulfate stimulated Hg methylation in low sulfate freshwater sediments. Experiments with pure cultures have verified the ability of SRB to catalyze MeHg production (Choi and Bartha, 1993; Choi et al., 1994). Recent studies have demonstrated that in addition to SRB, many other microbial groups including iron-reducing bacteria (Gilmour, 1996) could methylate Hg. Together, the above findings point to microbially-catalyzed methyl-Hg production in anaerobic bottom sediments as a major mechanism for MeHg input to waters and aquatic biota, except, perhaps in areas with other known sources of methyl-Hg input (eg. areas with high levels of methyl-Hg in precipitation (Rudd, 1995; Lindberg et al., 2001; 2005).

Net accumulation of methyl-Hg in aquatic systems is regulated by its relative rates of production and degradation (Oremland et al., 1991). Methyl-Hg can be decomposed in aquatic environments via two distinct microbially-catalyzed processes: (1) the mer operon-encoded organomercurial lyase/mercuric reductase detoxification system (Barkay, 1992), and (2) microbial catabolic pathways whose major functions are the metabolism of C1 compounds such as methanol (Oremland, 1991; 1995). The former process is generally thought to be associated mainly with aerobic bacteria inhabiting the water column in polluted systems in which Hg concentrations are sufficient to induce synthesis of the lyase and reductase enzymes (Barkay, 1992). In contrast, the latter process has been identified mainly as a sediment-borne phenomenon, which likely has an important influence on rates of sediment methyl-Hg production and release to the overlying water (Ramlal et al., 1986; Oremland et al., 1995). As with Hg methylation, studies have consistently shown that methyl-Hg decomposition in aquatic sediment is a

microbially-catalyzed process. Several different anaerobic microbial processes appear to be capable of catalyzing methyl-Hg decomposition in sediments, including  $\text{NO}_3^-$  reduction,  $\text{SO}_4^{2-}$  reduction, and methanogenesis. Methyl-Hg degradation by these processes is referred to collectively as “oxidative demethylation” (Oremland et al., 1991) since decomposition occurs in conjunction with metabolic processes associated with the organic carbon oxidation, which in most cases results in the oxidation of the methyl group to  $\text{CO}_2$ .

Methyl-Hg that accumulates in soils and sediments as net product of the concurrent processes of Hg methylation and methyl-Hg demethylation finds its way into living organisms and food chains via a combination of (1) direct absorption by diffusion through the lipid bilayer of cell membranes and (2) intake through diet. This aspect of the biogeochemistry of Hg is discussed later in relation with the impact of Hg on human health.

## **2.4 Mercury and Human Health Impacts**

### **2.4.1 Direct Exposure via Inhalation**

The forms of Hg of greatest health concern in gold mining by amalgamation are  $\text{Hg}^0$  (exposure by inhalation) and methyl-Hg (exposure via diet) (Shamely and Sack, 1989; Hentschel and Priester, 1992; Yasui et al., 1997; Stephen and Ahern, 2001; Valenzuela and Fytas, 2002; Hinton et al., 2003; Yokoo et al., 2003). Exposure could be direct inhalation of Hg vapor during the processing of the gold ore and refining of Au-Hg amalgam. The other possible source of inhalation comes from untreated wastewater emerging from processing directly discharged into water bodies (Harada et al., 1999; Akagi et al., 2000). At both historic and present AGM sites, miners hardly wear protective equipment such as face masks, respiratory protectors or gloves during the

amalgamation process and refining. Therefore, miners are/were Hg intoxicated (sleep disturbance, irritability, fatigue and excessive salivation). A few studies from North America, Australia and South Africa on Hg intoxication of miners in recent or past verify the incidents in historic mining centers (Shamely and Sack, 1989; Kippen, 1995; Donoghue, 1998; Fields, 2001; Stephen and Ahern, 2001; Eisler, 2003) unveiling what might have been the most disastrous and worst health impacts of Hg. However, the old Spanish literature is virtually silent on the ecological and health impacts (Nriagu, 1993). The extent of Hg's health impact on current SSM tropical miners, non-miners and the environment is virtually unknown in Africa, Asia or Latin America; though evidence of human contamination has been found at some sites in South America (Cleary and Thornton, 1994; Larceda and Salmons, 1998; Malm, 1998). Such studies are lacking in Ghana, hence the state of Hg health related problems are unknown.

#### **2.4.2 Exposure via Diet**

Accumulation of MeHg in fish and other aquatic organisms is the result of coupled biogeochemical and ecological processes. As mentioned earlier, the processes begin with the methylation of inorganic Hg, usually in anoxic sediments. Subsequent accumulation in biota occurs via bioconcentration and biomagnification through different trophic levels in aquatic food chain. Bioconcentration results from the uptake of methyl-Hg via diffusion across cell membranes (Rodgers and Bemish, 1982, 1983) and its rapid accumulation in tissues (Olson, 1986). Once inside cells, methyl-Hg binds strongly to sulfhydryl groups, hence allowing its accumulation in living tissues (Wood, 1983). Finally, because of its relative stability in biological systems, methyl-Hg is eliminated more slowly than the inorganic forms of Hg. Biomagnification, however, results from food intake across successive trophic levels (Watras and Bloom, 1992). Accordingly, the

higher the trophic level of a given species of fish, the greater the likelihood of it being contaminated with methyl-Hg via combined processes of bioconcentration and biomagnification. Thus, long-lived organisms such as the predatory fish are particularly prone to methyl-Hg contamination. The biomagnification factor of Hg in fish from different trophic levels shows quite a wide range of values (1 to approximately 6), but in all cases, fish tissue methyl-Hg concentrations are many orders of magnitude above levels in the surrounding waters (Watras and Bloom, 1992; Kim, 1995).

Humans contract Hg contamination on ingestion of Hg-contaminated fish. Methyl-Hg is rapidly absorbed from the gastrointestinal tract of humans due to its fast transport through biological membranes; which in association with tissue is very stable and is neither degraded nor excreted from the body at any significant rates. Consequently, methyl-Hg is accumulated by organisms through their lifetime (WHO, 1990; Barkay, 1992; US-EPA, 1997; Verity, 1997; Yasui et al., 1997; Clarkson, 2002; Yokoo et al., 2003). Methyl-Hg neurotoxicity is of concern, particularly to the developing fetus (Clarkson, 1994, 1995, 1997; US-EPA, 1997), and exposure to Hg by consumption of Hg-contaminated fish has been linked to neurological damage and myocardial infarction (Klein and Goldberg, 1970; D'Itri and D'Itri, 1977; Menkes, 1997; Verity, 1997; Nierenberg et al., 1998; Harris et al., 2003). Many studies have documented Hg levels in fish collected from Hg contaminated and non-impacted sites in the developed world, resulting in several posted fish consumption advisories (e.g., Ginsberg and Toal, 2000; Guide to Eating Sport Fish, 2003). By contrast, the levels of Hg in fish inhabiting water bodies impacted by AGM in developing nations remain poorly documented, and no fish

consumption advisories exist in these regions where subsistence fishing is the main source of proteins.

Following this overview of the environmental fate of Hg introduced to natural systems by anthropogenic activities, data obtained from the investigation of the impact of AGM by Hg amalgamation in a tropical river basin in Ghana are presented. AGM with Hg in Ghana accelerated after its legalization by the government in 1989. Now gold mining is scattered all over and covers about 50% of the nation (the Ghanaian gold belt). Unfortunately, both the impacts and fate of Hg used in the extraction of gold in this region remain poorly documented. The following three chapters represent studies on: (1) the quantification and speciation of Hg in different environmental compartments in the Pra River basin as well as AGM impacts on levels of other trace metals; (2) the ability of both soils and sediments collected from the Pra River basin to produce and accumulate methyl-Hg; and (3) the potential for solar radiation to enhance the production of methyl-Hg under tropical conditions (i.e. abundant organic matter and intense solar radiation).

## CHAPTER 3

### MERCURY IN DIFFERENT ENVIRONMENTAL COMPARTMENTS OF THE PRA RIVER BASIN, SOUTHWESTERN GHANA

#### 3.1 Introduction

In Ghana, small-scale gold mining (SSM) is defined as mining gold by any method not involving substantial expenditures by individual or group of persons not exceeding nine in number or cooperative society made up of ten or more persons (PNDC Law 218, 1989). Here, the SSM industry is believed to be over 2000 years old. This type of mining has traditionally played a significant role in the economy of Ghana. And since antiquity, the country has been one of the most important gold producers in Africa. Ghana earned the name “*Gold Coast*” when the Europeans arrived witnessing the land’s vast wealth of gold and the indigenous gold industry being manned by Ghanaians in their own simple way (Kesse, 1985; Hilson, 2001). The local population was the only miners of gold and diamonds in the traditional economy in 1471 before the European participation (Tsikata, 1997; Akabzaa and Darimani, 2001). Since then, the Hg-amalgamation technique has been used and is still being used to extract gold from crude ores of alluvial deposits in rivers and waterways and denuded outcrops and subsurface sediments along dried-up valleys (Dumett, 1998; Hilson, 2001). The application of the gold amalgamation technique continued until 1905 when the colonial authorities enacted a law making it illegal; therefore promulgated the Mercury law in 1933 banning Ghanaian gold miners from operating mining. Their operations remained illegal until 1989, when the government legalized SSM. Thus use of Hg to retrieve gold heightened and became



widespread in Ghana after legalization. Most of the gold produced by Hg-amalgamation in Ghana comes from goldfields located in the southwestern part of the country (Adimado and Baah, 2002). This Hg impacted geographical region is drained by three main rivers, which flow into the areas of intensive commercial fishing along the Gulf of Guinea. Currently, the SSM now is estimated to provide direct and indirect employment to over one million people and a potential source of income to the government (Akabzaa and Darimani, 2001; Hilson, 2001). It contributes about 10% of the annual tonnage of

Table 3-1. Mineral production from Ghanaian small-scale mining sector from 1989 to 2003

YEAR	SMALL-SCALE GOLD PRODUCTION (ounces)	PERCENT OF TOTAL NATIONAL GOLD PRODUCTION
1989	9,272	2.2
1990	17,234	3.2
1991	15,601	1.8
1992	17,297	1.7
1993	35,145	2.8
1994	89,520	6.3
1995	127,025	7.4
1996	112,349	7.0
1997	107,094	6.1
1998	128,335	5.8
1999	130,833	5.0
2000	145,663	6.0
2001	185,596	8.7
2002	160,879	7.2
2003	211,414	9.5

Source: Minerals Commission, Accra-Ghana, (2003).

gold (Table 3-1) with the remaining 90% coming from large-scale mining also located in the southwestern portion of the country (Adimado and Baah, 2002; Amankwa and Sackey, 2003). So gold is now the leading foreign exchange earner, bringing in over \$600

million annually to the nation, which represents about 45% of the total export revenue (Boroughs, 1997; Akabzaa and Darimani, 2001).

Artisanal gold mining (AGM), also known as ‘galamsey’ (gather and sell) in Ghana as in most developing countries, for decades is labeled as an informal industrial sector, employing thousands of people who adopt rudimentary, unmonitored and unregulated practices. Additionally, the partakers see it as the only means to prosperity coupled with others as exemplified in Chapter 1 (Meech et al., 1998; ILO, 1999). Similar to other AGM nations, in Ghana, the mining is a low technology, mainly labor-intensive peasantry now well regularized by mining laws and policies passed in 1989 (PNDCL 217, 218, 219). The AGM miners apply rudimentary methods mainly traditional/manual in winning gold, featuring simple tools like shovels, pick-axes, pans, chisels and hammers. The mining is classified as: shallow alluvial mining; deep alluvial mining; hard rock mining, and tailings from old workings. However, AGM miners are primarily involved in alluvial mining, as most of the river basins in Ghana are very rich in alluvium. Hence, a greater number of the activities of the AGM are performed in the rivers as well as the banks. The method of processing in any of the lists above is the same as described in chapter 2 (Figure 2-1). Amalgamation tailings are often left behind forming Hg “hot spots” in both terrestrial and aquatic ecosystems as mentioned in Chapter 2. Some also end up in ponds and domestic water wells. The Hg rich tailings remaining in most mining sites subsequently become susceptible to leaching, erosion and volatilization. The high organic matter content in tropical aquatic and terrestrial environments also favors metallic Hg transformation by either biotic or abiotic pathways into MeHg (Kehrig et al., 1997; Meech et al., 1998; Larceda and Solomons, 1998). Today

the results of these activities are obvious-extensive environmental damage, ecosystem degradation, loss of biodiversity and the potential release of other heavy metals from the rock strata as observed elsewhere (Amegbey et al., 1997; Addy, 1998; Larceda and Salomons, 1998; Hilson, 2002a, b; Villas Boas et al., 2001; Hinton et al., 2003; Maponga and Ngorima, 2003).

Apparently this type of mining has come to stay as observed in other gold-rich developing nations. In this regard, several scientific studies on Hg transport to water bodies, its transformation to the more toxic and readily bioavailable methyl-Hg (MeHg), contamination of food chains, and human exposure have been carried out in historic sites in USA and Canada (Bonzongo et al., 1994, 1996; Miller et al, 1995; Chen et al., 1997) and Latin America especially the Brazilian Amazon (e.g. Villas Boas, 1997; Malm, 1998; Meech et al., 1998; Laceda and Salomons, 1998; Lechler et al., 2000). Nevertheless, there is relatively little to no published information based on reliable Hg data for most of Africa, particularly Ghana, with the exception of Tanzania, Zimbabwe (Ikingura and Akagi, 1996; Ikingura et al., 1997; van Staaten, 2000a,b), and recently some preliminary data for Kenya and Uganda (Campbell et al., 2003a,b,c; Igola et al., 2002). So far there have been only few preliminary data reports on Hg levels in surface water, sediments, soils and some staple foods from the Ghanaian gold belt in the southwest. Adimado and Baah (2002) studied Hg concentrations in human tissues and fish from Ankobra and the Tano river basins. Bannerman et al. (2003) recently reported a snapshot on Hg and arsenic (As) in sediment and water in the gold mining areas of the Ankobra river basin. Also brief studies on Hg in water, sediments and soil of some rivers near Dunkwa-On-Offin were carried out (Golow and Mingle, 2002; Golow and Adzei, 2003). In addition,

Amonoo-Niezer et al. (1996) investigated Hg and As pollution on soils, food crops and fish in the environs of the mining town of Obuasi. Lately, Hg studies were performed by Babut et al. (2003) on water, sediment, soil and food crops in Apopre stream, at Dumasi (a well-known *galamsey* town), supported by the United Nations Industrial Development Organization (UNIDO); Bonzongo et al., (2003, 2004) also examined the extent of Hg contamination in water, sediment and soil from selected mining-impacted Ghanaian watersheds; and Nartey et al. (2004) investigated Hg pollution in some gold mining communities in Ghana. Most of the aforementioned publications suffer from limitations related to use of inadequate sampling and handling techniques and rarely used the recommended state-of-the art “ultra-clean free-metal sampling protocol” (e.g. Gill and Fitzgerald, 1985). The literature documents that studies where ultra trace methods were not used, published data were characterized by inaccuracies (Fitzgerald et al., 1998). These facts then raise doubts and uncertainties in the quality of data reported on Hg in the various environmental compartments in Ghana to date. Further, there has not been any comprehensive and in-depth study to unveil the state of Hg levels and impacts in the various environmental compartments in the main river basins where alluvial gold is mined in the past or present. Therefore, no data exist for any of these major rivers, such as the Pra River basin, the focus of this study. As such, the health implications remain largely unknown, and currently SSM is practiced extensively in the southwest, central and northern parts of the country (Hilson, 2002).

The objectives of this research were: (1) to document the levels and speciation of Hg in different environmental compartments within the Pra River basin in southwestern Ghana; and (2) to assess the potential impact of AGM in this river basin.

### 3.2 Study Site

Ghana is located in Africa (Figure 3-1), along the Gulf of Guinea. It is roughly rectangular in shape with an area of 239,460 square kilometers (Kesse, 1985). It lies between latitude  $4^{\circ} 44' N$  at Cape Three Points in the south and latitude  $11^{\circ} 44' N$  in the north. The country's eastern and western outmost parts lie at longitudes  $3^{\circ} 15' W$  and  $1^{\circ} 12' E$ . Its coast line is 555 kilometers (Km) long and is cut by the Greenwich Meridian at Tema 24 Km to the east of the capital Accra. Ghana is bounded in the east by the Republic of Togo, on the west, is Ivory Coast and on the north, is Republic of Burkina Faso (Kesse, 1985). The climate is tropical and humid in the southern part of the country with an average variable temperature of  $24^{\circ}C$  to  $28^{\circ}C$ . The northern part, though tropical, is dry and mostly falls within the Sahelian zone (Kesse, 1980).

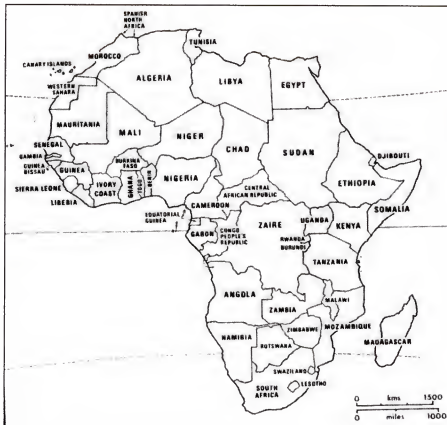


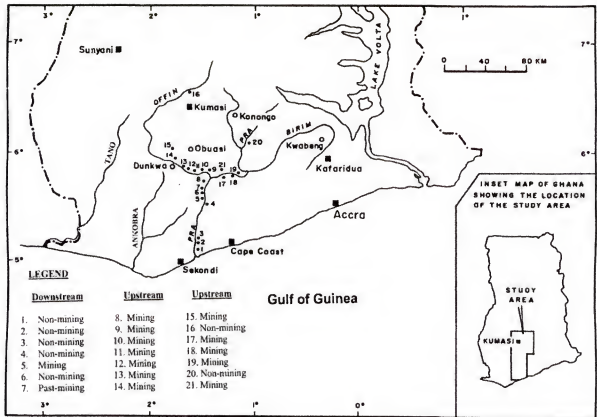
Figure 3-1. Map of Africa showing the location of Ghana.

The study area is the southwestern part of Ghana where most of the gold mines are located, representing an area of 40,000 Km<sup>2</sup>. In this region, the geology is predominantly Precambrian rock - the Birimian and Tarkwaian formations (Kesse, 1985; Dumett, 1998). These rocks are found in the Eastern, Central and Western regions as well as Ashanti region. The Precambrian rocks are believed to have resulted from folding, faulting, metamorphism, igneous activity erosion and sedimentary processes, giving birth to the current gold belts that exist today, covering approximately one-sixth of the surface area of the country. The first group of belts, ranging between 15 and 40 km in width, accommodates Birimian gold, extending from Ghana westward into Senegal and Mauritania, and northward into Burkina Faso. The Birimian occupies about 20% of the total area of Ghana. These belts are richly endowed with Proterozoic greenstone-type gold lode deposits that are highly variable featuring gold that occurs in both quartz-filled shear zones and within altered rocks adjacent to shear zones (Kesse, 1985; Leube et al., 1990; Taylor et al., 1992; Mumin, 1994; Hilson, 2002).

The second group is the Tarkwaian system, which is concentrated mainly in the southwestern part of Ghana. The belt stretches from near Axim in the Western Region to the edge of the Volta basin. The Tarkwaian is thought to have been derived from the Birimian and associated granitoids through deposition (Kesse, 1985). Additionally, the Tarkwaian clastic sediments overlie the Birimian unconformably (Kesse, 1985). This class has Tarkwaian gold: auriferous quartz-pebble conglomerate deposits- quintessentially, a matrix of fine-grained quartz and black sands (mainly hematite, and to a lesser extent, ilmenite, magnetite and rutile) (Kesse, 1985; Leube et al., 1990; Dzignbodi-Adjimah, 1995; Mumin, 1994; Klemd et al., 1993; Hilson, 2002). Thus, a large

portion of southwestern Ghana, because of erosional events, parts of these different rocks have been re-deposited as placer gold deposits, also called “alluvial gold”. These are found in many of the rivers draining Birimian rocks or the gold belt particularly the three major rivers: Pra (18, 734 Km<sup>2</sup> basin) and its tributaries, Ankobra (7, 148 Km<sup>2</sup>), and Tano (13, 694 Km<sup>2</sup> basin) (Figure 3-2) (Oberthur et al., 1997; Hilson, 2001; Adimado and Baah, 2002; Hilson, 2002).

The investigation was conducted along the Pra River, which takes its source from Kwahu Plateau before joining by the main tributaries rivers Offin and Birim (Figure 3-2) to enter the Gulf of Guinea. Nearly the entire Pra basin is a very active AGM site. Inevitably, Hg from processed wastes is released to rivers and mine tailings, resulting in significant widespread environmental contamination in this part of Ghana. The contamination in this river basin is further exacerbated by high annual precipitation and very active fluvial processes characteristics of tropical regions. Accordingly, Hg transported from river upstream reaches would: (i) contaminate water and fish that serve as drinking water and food resources for the communities along its course (ii) deteriorate water quality and (iii) accumulate in the river’s estuary and the Gulf of Guinea, two areas of intensive commercial fishing.



Source: Survey Dept., Accra-Ghana

Figure 3-2. Map of the gold mining impacted southwestern Ghana region showing sampling locations on the Pra River and its tributaries-site 1 is the farthest downstream with the numbering increasing upward.

### 3.3 Methods and Materials

#### 3.3.1 Sampling

During the rainy season of 2002 and the dry season of 2003 in Ghana (Figure 3-3), water, sediments, soils, and human hair were collected along longitudinal transects in the Pra River and its watershed, (Figure 3-2 sampling sites are marked in numerals. The legend defines the sites). Samples were collected from 21 sites including locations near



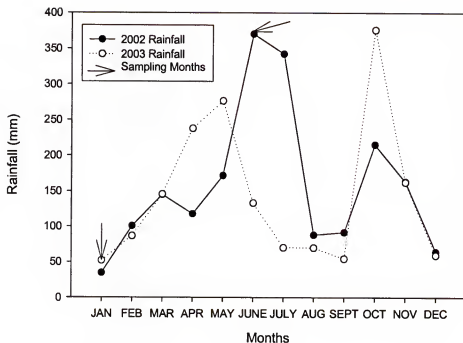


Figure 3-3. Monthly rainfall (mm) distribution at Assin Fosu, close to the Pra River Basin. The black dots are the rainy months for 2002 and the open dots are for 2003. The arrows indicate the months in which sampling was done.

sites of either past or current AGM sites (sites 5-15, 17, 18, 19, and 21 upstream) and from locations remote from known mining centers (sites 1-4, downstream) such as headwaters (sites 16 and 20) to assess the extent and level of Hg contamination related to this activity. The 21 sampling sites were selected on the Offin, the Upper Pra, and the Lower Pra (Figure 3-2). From these sites, surface water samples were collected from headwaters upstream of mining sites to near the river delta. Sampling sites also included points of connection between streams and canals connecting mining sites/ponds to the Pra basin. Water samples were collected directly into acid pre-cleaned Teflon<sup>®</sup> bottles (0.5% optima HCl), using the “ultra-clean free-metal sampling” protocol (Gill and Fitzgerald 1985; 1987). Additional water samples were also collected in pre-cleaned polyethylene bottles for the determination of major ions and dissolved organic carbon (DOC). Surface

sediment samples (0 to 10cm) were taken from sites of water collection and placed in acid pre-cleaned polyethylene containers by manual scooping employing Teflon spoon. Soil samples were also taken from some mining and amalgamation sites, amalgam roasting points, and from sites away from mining centers along the river. The pH and water temperature were measured in the field using a portable pH meter and Mercury – in – glass thermometer, respectively.

Two types of biological samples were collected. First, hair samples were cut close to the rear of the scalp of each individual who volunteered at selected sites (Tables 3-12 and 3-13). Hair samples were obtained from 53 people including 2 females during the rainy season, and only 7 in the dry period from one site. The majority of the samples were from the miners, whereas the remaining were from people living in riverine villages, having little or no direct contact with gold mining activities. It was extremely difficult to obtain hair samples because of superstition especially in the dry season. Details of age, occupation, and location of residence were also compiled during sampling resulting in easier assessment of occupational and residential exposure. Other information concerning dietary habits of the volunteers was also collected using an interview-administered questionnaire. The questions covered fish consumption, stressing the most frequently consumed fish during high and low flow regimes of the year. Secondly, smoked fish samples were purchased directly from local fishermen during the dry season only. In general, fish is smoked in most fishing areas of Ghana for preservation, storage and ease of transportation purposes. The selected species were those considered the most important to the local population's diet and consumed most of the year. Obtained fish samples were weighed, measured, and identified (e.g., scientific name) in the biology

Department at the University of Ghana. All collected samples were stored frozen at the University of Ghana, Accra before being shipped by express courier to the laboratory at the University of Florida, Gainesville where all analyses were conducted.

### **3.3.2 Sample analysis**

#### **3.3.2.1 Total and methyl-Hg in the aqueous phase**

Total-Hg (THg) concentrations in non-filtered water were determined after subjecting a known volume of a water sample to  $\text{BrCl}/\text{SnCl}_2$ , followed by gas-phase purging with Hg-free  $\text{N}_2$  and trapping of  $\text{Hg}^0$  onto gold-coated sand (Bloom and Crecelius 1983). The  $\text{Hg}^0$  was then thermally desorbed from the gold trap in stream of Hg-free helium and quantified by CV-AFS. Methyl-Hg (MeHg) was determined by direct ethylation of the water using sodium tetraethylborate, followed by CV-AFS detection after GC-separation and thermal decomposition of the alkyl-Hg.

Due to the lack of an ultra clean facility at the University of Ghana, water samples could not be filtered soon after collection. Therefore, only non-filtered data are presented.

#### **3.3.2.2 Total and methyl-Hg in sediments and soils**

Before analysis, sediment and soil samples were freeze-dried and sieved, and the < 63  $\mu\text{m}$  fraction (about 0.5g) was used for digestion with a  $\text{HCl}:\text{HNO}_3:\text{HF}$  acid mixtures in a closed Teflon vessel overnight at 110°C (Hossner, 1996; Bertsch and Bloom, 1996). The mixture on cooling was diluted with saturated solution of  $\text{H}_3\text{BO}_3$  to dissolve the fluorides, then filtered (0.45 $\mu\text{m}$ ). Aliquots of the digestate were analyzed for total Hg by CV-AFS after  $\text{SnCl}_2$  reduction, gold trapping and detection by AFS. MeHg was released from sediment and soil samples after alkaline digestion with 12 % KOH in methanol in a closed Teflon vials at 75°C overnight and analyzed by CV-AFS after subjecting the

samples to aqueous phase ethylation, GC separation and thermal decomposition (Horvat et al. 1994).

For QA/QC purposes, reagent blanks and certified reference material (CRM), IAEA-405 for estuarine sediments obtained from the International Atomic Energy Agency (IAEA), were run with all THg and MeHg digestions/analyses. Recoveries on IAEA-405 averaged  $98 \pm 7\%$  for total-Hg ( $n=7$ ) and  $91\%$  for methyl-Hg ( $n=8$ ). Recoveries on matrix spikes ranged from 90-105% for both THg and MeHg. Appendix A shows the efficiency of the used techniques to recover THg and MeHg from the CRM over time.

### **3.3.2.3 Total and methyl-Hg in fish**

Fish THg and MeHg contents were determined according to the procedure developed by Bloom (1989, 1992). For THg, about 1.00g of fish sample was digested with  $\text{HNO}_3\text{-H}_2\text{SO}_4$  overnight, and analyzed by CV-AFS after  $\text{SnCl}_2$  reduction. In the case of MeHg, samples of about 0.5g each were placed in Teflon vials with 15 ml of 25% KOH in methanol, shaken vigorously and allowed to digest in an oven at  $70^\circ\text{C}$  overnight. Samples were then analyzed by aqueous phase ethylation, cryogenic GC separation and CV-AFS detection. Accuracy was determined by the analysis of certified reference material (DORM 2, National Research Council, Canada with a THg concentration of  $4.64 \pm 0.26$  mg/kg and MeHg mean concentration of  $4.47 \pm 0.32$  mg/kg. Averaged recoveries were  $4.55 \pm 0.16$  ( $n = 6$ ) and  $4.38 \pm 0.09$  ( $n = 6$ ) for THg and MeHg, respectively.

### **3.3.2.4 Total and methyl-Hg in hair**

Hair samples were first washed with DI-water and air-dried. For THg determinations, about 50mg were then digested overnight at  $80\text{-}90^\circ\text{C}$  using  $\text{HNO}_3$  (Akagi et al, 1995). For MeHg, about 100mg of hair was added to 2 ml of 5M  $\text{HNO}_3$  in a Teflon bomb and heated at  $100^\circ\text{C}$  for 200 minutes (Diéz and Bayona, 2002; Montuori et al.,

2004). An aliquot of cooled digestate was transferred to a Teflon bubbler with 60 ml nanopure water. The mixture was buffered with an acetate buffer solution ( $\text{pH} = 4.5$ ) and ethylated using sodium tetraethylborate (Bloom, 1989). MeHg was determined after GC-separation and thermo-decomposition by atomic fluorescence spectrometer. For hair samples, a human hair certified reference material (IAEA-086) with a THg concentration of 0.573 mg/kg and MeHg average concentration of 0.258 mg/kg was analyzed in conjunction with the samples. Average recoveries were  $98 \pm 8\%$  and  $93 \pm 3\%$  for THg and MeHg, respectively.

### **3.3.2.5 Determination of other trace metals by ICP-AES**

For total metal analysis besides Hg in the sediments (3.3.2.2), samples were analyzed for total concentrations of Al, Fe, As, Pb, Cu, Cr, Ni, Mn, Co, V, and Zn by inductively coupled plasma-atomic emission spectrometer (ICP-AES). The data obtained are averages of triplicate analysis of a single digested sample. Simple linear regressions and 95% confidence intervals were used to (i) identify sites with metal concentrations above background values based on co-variation with aluminum; and (ii) examine the relationship between any two of the investigated metals.

### **3.3.2.6 Determination of dissolved organic carbon and solid organic matter**

Dissolved organic carbon (DOC) in water was measured by high temperature catalytic combustion using a Tekmar-Dohrmann Apollo 9000 HS Combustion TOC Analyzer. Total organic carbon content in soil and sediment samples was measured as loss on ignition (LOI) by ashing at  $550^{\circ}\text{C}$  for 2 hours.

### **3.3.2.7 Determination of major ions in the aqueous phase**

Dissolved major ions were also determined on non-acidified filtered ( $0.45\mu\text{m}$ ) water samples by ion chromatography (Welch et al. 1996).

### 3-4. Results and Discussion

#### 3-4.1. Mercury in the aqueous phase

Concentrations of THg and MeHg determined on samples collected during both the rainy and dry seasons are presented in Table 3-2. In both seasons, trends in THg concentrations show peak values corresponding primarily to points of Hg inputs by active and past mining activities at sites 5, 7, 9-19 and 21. High THg concentrations were also recorded at the non-mining sites (sites 1-4) downstream, as shown in Figure 3-2. Based on lack of signs of either current or past mining activities in the headwaters of the studied system, a low background value was anticipated from sites 16 on the Offin River and 20 on the Upper Pra (Figure 3-2). Surprisingly, in both the rainy and dry seasons, THg data obtained from these specific sites were amongst the highest measured values, clear evidence of contamination that is likely attributable to historic mining. In a preliminary investigation of the wider southwestern Ghana (Bonzongo et al., 2004), water samples collected from a control site (i.e. not directly impacted by mining activities) had a THg concentration of  $3.22 \text{ ng L}^{-1}$ , which is within the range of most reported baseline values from different non-contaminated aquatic systems (e.g., Gill and Bruland 1990; Bonzongo et al. 1996; Lyons et al. 1999). In fact, all sampled sections of the Pra River system in this study are obviously contaminated with Hg, and the mean THg concentrations in this river system are 1 to 2 orders of magnitude higher than those found in most uncontaminated rivers. Measured THg concentrations in the Pra River waters ranged from 28.7 to 420.3  $\text{ng L}^{-1}$  in the rainy season and from 45.2 to 462.1  $\text{ng L}^{-1}$  in the dry season (Table 3-2). When sites are considered individually, THg values decrease or increase with the shift from rainy to dry season. Without total suspended solid (TSS) data (not measured), one can only speculate that peak values in the rainy season are likely due to inputs of Hg

contaminated particles from run-offs as reflected by the observed highly turbid surface waters, while during the dry season, high THg levels are sustained by the increase in mining activities that are usually less intensive in the rainy season due to frequent flooding.

Unlike the THg values discussed above, MeHg concentrations show a clear decline from the rainy to the dry season, and during the dry season, a few samples had MeHg levels below the analytical detection limit of  $\sim 0.028 \text{ ng L}^{-1}$ . Thus measured MeHg in surface waters during the rainy season is predominantly believed to emerge from terrestrial sources, and is introduced into surface river waters via soil erosion and run-offs. However, in the dry season, the terrestrial source either ceases or minimizes, and measured MeHg probably originates predominantly from in-river production, supplemented by any other potential sources such as groundwater inputs. This observation is supported in part by the DOC data (Table 3-2). During the rainy season, DOC concentrations were higher than in the dry season presumably due to terrestrial organic matter inputs from the heavily vegetated watershed of the studied river system. The latter then translates into high DOC in the aqueous phase despite the high dilution effect caused by torrential rains characteristics of Southern Ghana. Overall, DOC values decrease at nearly all sites during the dry season, supporting the above-stated hypothetical explanation. It is worth noting that MeHg determined on the water samples is not the total extractable MeHg. Since neither distillation nor a chemical extraction was conducted prior to sample ethylation, measured MeHg is operationally defined here as labile MeHg. This avoids the recently reported analytical artifacts associated with MeHg

separation from the sample matrix with high inorganic Hg and organic matter concentrations (e.g. Bloom et al., 1997). Therefore, values listed as <0.028 in Table 3-2 could simply correspond to the lack of labile MeHg. Lastly, no correlation was observed between measured DOC and THg or MeHg in either season.

Table 3-2. Concentrations of total-Hg (THg), methyl-Hg (MeHg), and dissolved organic carbon (DOC) in water samples collected during June 2002 rainy and January 2003 dry periods. (nd = not determined)

Pra River System		Total-Hg		Methyl-Hg		DOC	
River sections	Sites #	Rainy ng L <sup>-1</sup>	Dry ng L <sup>-1</sup>	Rainy ng L <sup>-1</sup>	Dry ng L <sup>-1</sup>	Rainy mg L <sup>-1</sup>	Dry mg L <sup>-1</sup>
Lower Pra	1	295.7	171.3	2.59	<0.028	10.48	3.26
	2	233.6	99.0	19.64	0.80	13.39	6.39
	3	52.0	71.7	2.29	<0.028	21.62	6.87
	4	29.1	104.4	1.15	<0.028	11.65	6.70
	5	403.0	100.4	0.69	0.40	5.18	6.79
	6	28.7	92.8	0.95	0.40	13.67	6.50
	7	34.4	nd	1.86	nd	11.45	nd
	8	36.1	57.2	2.65	0.60	11.07	6.67
Offin	9	420.3	169.1	1.57	<0.028	12.58	7.84
	10	91.8	225.6	1.59	0.68	16.79	7.23
	11	348.6	373.3	1.20	<0.028	14.46	7.65
	12	230.1	308.5	3.08	0.71	5.71	6.65
	13	84.6	249.6	1.97	0.82	13.82	7.50
	14	41.6	182.4	1.79	0.49	7.12	7.64



Table 3-2. Continued

Pra River System		Total-Hg		Methyl-Hg		DOC	
	15	220.5	462.1	1.87	0.51	10.88	3.14
	16	148.9	79.8	1.23	0.47	15.31	6.74
	17	41.5	188.0	0.88	<0.028	10.08	6.78
	18	69.3	52.7	<0.028	0.59	9.37	6.91
Upper Pra/Birim	19	136	45.8	0.93	0.45	4.46	11.61
	20	293.5	118.2	0.99	0.78	10.11	6.74
	21	210.7	84.7	1.03	0.70	8.33	6.17
<i>Average</i>	-	164.28	161.83	2.378	0.420	11.31	6.79
<i>Median</i>	-	136.00	111.30	1.570	0.480	11.07	6.76
<i>Maximum</i>	-	420.30	462.10	19.640	0.820	21.62	11.61
<i>Minimum</i>	-	28.70	45.80	0.000	0.000	4.46	3.14

Further, Hg, when compared with available safe guidelines for water consumption on one hand and THg levels in tropical river systems impacted by similar AGM activities on the other hand, the following trends are observed: First, THg levels in waters of the Pra river system do not exceed the 1  $\mu\text{g L}^{-1}$  or the 2  $\mu\text{g L}^{-1}$  levels for drinking water set by the World Health Organization (WHO, 1976) and the US-EPA, respectively.

However, all obtained values exceed the 12  $\text{ng L}^{-1}$  standard set by the US-EPA for protection against chronic effects to aquatic wildlife (US-EPA, 1985). Secondly, THg concentrations determined in the Pra River waters are higher than those reported for most Hg-contaminated sites in the Brazilian Amazon and Indonesia. For instance, while THg values in the Pra river system average 164.28 and 161.83  $\text{ng L}^{-1}$  for the wet and dry seasons, respectively, far lower values have been reported for the Madeira and the Tapajos rivers in Brazil, averaging 9.51 and 3.4  $\text{ng L}^{-1}$ , respectively (Cleary et al., 1994; Malm et al., 1990; Lechler et al., 2000; Bonzongo et al., 2002). A similar trend is observed with data reported for some Indonesian sites, averaging 6.03  $\text{ng L}^{-1}$  (Aspinall,

2001). In contrast, THg values reported from AGM-impacted sites on Mindanao Island in the Philippines are several orders of magnitude higher than numbers obtained from any of the above-mentioned Pra sites and average 75,400 ng L<sup>-1</sup> (Appelton et al., 1999; Akagi et al., 2000; Drasch et al., 2001). Likewise, in Tanzania in East Africa, the mean THg value is 680 ng L<sup>-1</sup> (Ikingura et al., 1996), four times higher than that of Ghana. Further comparing with impacted historic mining site like the Carson River (USA) (Bonzongo et al., 2002), the mean value of the Ghanaian river basin is lower than that of the Carson River (average: 429.2 ng/l). The observed differences between the Ghanaian river basin and the other AGM sites could be attributed to the period of sampling, the number of sites and distances from points of collection as well as the amount of Hg released during amalgamation and roasting of Hg (Bonzongo et al., 2004). In the case of MeHg, contrasting with the well studied Hg-impacted Madeira and Tapajós Rivers and the Carson River, concentrations measured in samples collected from the Pra river basin are far higher. With regard to the longitudinal distribution of both THg and MeHg, unlike most impacted river systems that show a general decrease downstream from main points of Hg introduction to the river (Bonzongo et al., 2002), the Pra River and its tributaries have several and unequally distributed past and current mining sites resulting in a rather peculiar Hg distribution from headwaters to the most downstream reaches. Finally, other water quality parameters measured did not show any significant impact on Hg concentrations in the river basin. However, most major ions measured showed a higher concentrations during the low flow period; and the pH of the water(s) from the basin was fairly constant along the river during both seasons, averaging 6.5 (wet period) and 6.7 (dry period), likewise temperature (Appendix A).

### 3-4.2. Mercury in Sediments

Total and methyl Hg concentrations determined on surface sediment samples collected during both the rainy and dry seasons from the 21 sites along the Pra River system are presented in Table 3-3 and compared graphically, (Figure 3-4). Elevated concentrations of Hg were observed in samples collected from sites downstream of active mining centers, located a few or several kilometers away from mining centers (sites 1 through 4 and 6). The higher peaks observed near mining sites (upstream or downstream) reveal Hg concentration diminishes suggesting that Hg contaminated particles is preferentially deposited close to the source of contamination, and also demonstrating the impact of AGM activity on sediment quality (Figures 3-2 and 3-4). A case in point compares site 8 with sites 7 and 9 in the rainy period, Figure 3-2. The non-mining centers

Table 3-3. Total and methyl-Hg concentrations in mg/kg in sediments samples collected during the June 2002 rainy and January 2003 dry periods.

Pra River System		Total-Hg		Methyl-Hg		Organic Matter as	
River sections	Sites #	Rainy	Dry	Rainy	Dry	Rainy	Dry
		mg Kg <sup>-1</sup>	mg Kg <sup>-1</sup>	mg Kg <sup>-1</sup>	mg Kg <sup>-1</sup>	%	%
Lower Pra	1	0.076	0.003	0.040	<0.001	2.08	0.46
	2	0.076	0.008	0.046	<0.001	5.55	3.15
	3	2.917	0.002	0.023	<0.001	9.98	1.68
	4	0.018	0.017	0.007	<0.001	11.50	4.74
	5	0.046	0.005	0.018	<0.001	1.30	0.25
	6	0.103	0.043	0.010	0.001	4.92	0.96
	7	0.022	0.009	0.015	<i>nd</i>	1.67	<i>nd</i>
	8	0.310	0.002	0.015	0.001	7.61	3.01

Table 3-3. Continued

Pra River System		Total-Hg		Methyl-Hg		Organic Matter as	
River sections	Sites #	Rainy mg Kg <sup>-1</sup>	Dry mg Kg <sup>-1</sup>	Rainy mg Kg <sup>-1</sup>	Dry mg Kg <sup>-1</sup>	Rainy %	Dry %
Offin	9	0.032	0.008	0.002	0.001	0.59	0.46
	10	0.022	0.007	0.003	<0.001	0.28	0.40
	11	0.132	0.118	0.048	<0.001	1.50	0.47
	12	0.329	0.026	0.009	<0.001	2.62	2.48
	13	0.032	0.007	0.015	<0.001	0.62	0.53
	14	0.121	0.018	0.040	<0.001	1.79	0.47
	15	0.072	0.036	0.009	<0.001	6.53	2.79
	16	0.189	0.010	0.075	<0.001	6.85	4.39
Upper Pra/Birim	17	0.079	0.002	0.018	<0.001	1.91	1.74
	18	0.678	0.002	0.028	<0.001	2.89	0.52
	19	0.071	0.005	0.007	<0.001	1.56	0.39
	20	0.180	0.030	0.003	0.005	7.91	0.84
	21	0.070	0.043	0.005	0.005	3.47	2.91
<i>Average</i>	-	0.265	0.019	0.021	0.001	3.96	1.63
<i>Median</i>	-	0.077	0.008	0.015	0.000	2.62	0.84
<i>Maximum</i>	-	2.917	0.118	0.075	0.005	11.50	4.74
<i>Minimum</i>	-	0.018	0.002	0.002	<0.001	0.280	0.25

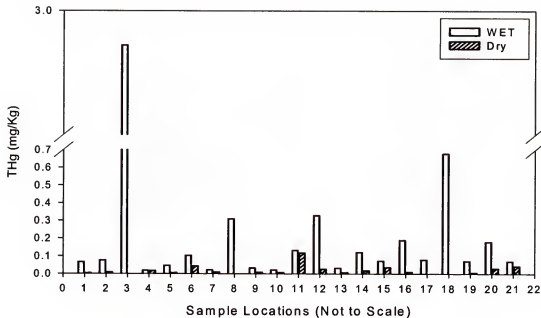


Figure 3-4. Longitudinal distribution of total-Hg concentrations (ppm) in surface sediments collected from the Pra River Basin during June 2002 wet and January 2003 dry seasons.

also show a similar pattern. Therefore, increased run-off during the rainy season does accelerate the transport of Hg contaminated particles into the stream bed, verifying the observed higher values downstream, sites 1-3. In the dry season, sediments are less enriched with fines. As a consequence, much lower THg values were observed in samples collected during the dry season. With the exception of four samples collected during the rainy from sites 3, 8, 12, and 18, none of the other measured Hg concentrations exceeded the US-EPA (1985) quality guideline of  $0.2 \text{ mg Kg}^{-1}$ . One possibility could be that the local THg background in geological material is naturally very low. This is supported by the very limited number of THg data on sediment from sites not directly impacted by mining activities. The assessment of deviation of measured THg concentrations in sediments from background values is discussed together with other heavy metals in the subsequent sections. Generally, THg values were higher in samples

collected during the rainy season than the dry season, when inputs of Hg-contaminated particles into the river were high, resulting in increased sediment Hg-levels. In addition, high river flow regimes characteristics of the rainy seasons in this tropical region produce sediment re-suspension resulting in downstream transport of Hg-contaminated fine sediment particles, thus distinguishing the different flow regimes.

Finally, comparing Ghana's sediment THg data with those obtained from some of the well-studied AGM-impacted sites and well known contaminated historic mining sites (e.g. the Carson River in Nevada) discussed earlier (section 3-4.1), the average THg concentrations of 0.265 and 0.019 mg Kg<sup>-1</sup> for wet and dry seasons, respectively, in the Pra River system were far lower than the reported 21.03 mg Kg<sup>-1</sup> for the Philippines' sites and the range of 2.0-156 mg Kg<sup>-1</sup> for Carson River. Nevertheless, the Ghanaian mean values compared quite well with some of the numbers reported for the Mairader River (average: 0.04 mg Kg<sup>-1</sup>) and the Tapajós River (average: 0.29 mg Kg<sup>-1</sup>) in the Brazilian Amazon (e.g. Malm, 1990; Malm, 1998; Lodenius and Malm, 1998). Several factors could account for the observed differences in THg concentration as discussed in the aqueous phase (3-4.1, such as, the magnitude of AGM activities, volume and flux of waterways and sediment grain size (Larceda and Salmons, 1998). Moreover, these data from the Pra river seem to be on the low end for sites that have been supposedly exposed to AGM by Hg amalgamation for centuries. A few previous studies (e.g. Bonzongo et al., 2004; Nartey et al., 2004) recently conducted in the same watershed found broader ranges and higher levels of THg in water, sediments, and soils, when samples collected from mining ponds and canals connecting these ponds to rivers were included. Lastly, and similar to the trend observed in the aqueous phase, MeHg levels in sediments were higher

than most values reported for sites with similar climate and impacted by artisanal gold mining as well as other known historic sites in North America (e. g., Domagalski, 2001; Gray et al., 2000)

Sediment organic matter content followed a similar trend, in that high OM content is associated with the rainy season and low values with the dry season. Of interest is the trend of MeHg concentrations between seasons. While THg in samples collected during the wet season contained ~1 to >68% MeHg, the methylated Hg fraction was barely detectable in most of the samples collected during the dry period. Similar to the water data discussed earlier, the belief is that the higher MeHg concentrations observed in surface sediments during the wet period are likely due to terrestrial inputs, perhaps in combination with a limited in-river sediment production. Laboratory experiments were used to verify this hypothesis, and obtained data are discussed in Chapter 4.

### **3.4.3 Impact of AGM on Levels of Trace Elements other than Mercury in Sediments**

Seasonal variations of the total concentrations of the other metals are summarized in Tables 3-4 (wet season) and 3-5 (dry season). Al, Fe and Mn had higher concentrations than the rest of the elements examined. As and Pb behaved similarly during the rainy season, but in the dry season, Pb concentrations were below the analytical detection limit at all sites. Zn, Cu, Co, Ni, V and Cr exhibited their highest concentrations in the sediment during the high flow regime. Cobalt, like Pb, was below detection limit during low flow regime (Table 3-5). The correlation matrix amongst investigated metals (Tables 3-6 and 3-7) points to: (i) the lack of relationship between organic matter (%OM) and all analyzed metals in both the dry and wet seasons; (ii) strong and significant correlations between Al and Fe, Cu, Ni, V, Cr, and Zn in the dry season; (iii) weaker but significant relationships between Al and Fe, Cu, Mn, Co, Ni, and Cr in the rainy season. The lack of

strong correlation between OM and any of the analyzed metals indicated that a significant fraction of the metals of interest in the sediments was associated with fine inorganic particles. This observation allowed the use of Al as a normalizer in determining the contamination state of the Pra River sediments as discussed below.



Table 3-4: Total metal concentrations in mg/kg dry weight (ppm) and organic matter content determined as loss on ignition (LOI) on river sediments collected from the Pra River basin during "June 2002 rainy season".

River	Section	Site #	Hg	Al	Fe	As	Pb	Cu	Mn	Co	Ni	V	Cr	Zn	% OM
Lower Pra		1	0.066	278.1	301.2	0.414	0.238	0.263	6.790	0.053	0.439	0.777	0.905	1.418	2.08
		2	0.076	267.5	328.1	0.411	0.043	0.226	8.955	0.134	0.370	0.791	0.819	1.531	5.55
		3	2.917	236.9	168.7	0.213	0.179	0.252	2.387	0.130	0.271	0.706	0.724	1.553	9.98
		4	0.018	146.2	134.8	0.184	0.064	0.127	3.516	0.063	0.308	0.392	0.47	0.742	11.50
		5	0.046	174.7	225.3	0.360	0.096	0.221	6.518	0.188	0.362	0.758	0.825	1.214	1.30
		6	0.103	195.1	155.6	0.384	0.041	0.158	4.384	0.078	0.318	0.518	0.586	0.754	4.92
		7	0.022	223.6	220.7	0.488	0.022	0.221	6.297	0.166	0.348	0.652	0.744	1.072	1.67
		8	0.310	348.9	370.4	0.691	0.078	0.333	8.595	0.272	0.493	1.098	1.321	1.285	7.61
Offin		9	0.032	172.2	224.9	0.12	0.051	0.206	1.174	0.335	0.406	0.693	0.640	5.906	0.59
		10	0.022	55.9	103.4	0.395	0.071	0.153	1.488	0.062	0.249	0.349	0.396	1.685	0.28
		11	0.132	236.8	190.9	0.714	0.017	0.227	0.940	0.230	0.346	0.749	0.775	4.199	1.50
		12	0.329	317.6	328.1	4.31	0.038	0.877	1.401	0.288	0.489	1.274	1.261	5.486	2.62
		13	0.032	178.0	143.9	0.100	0.112	0.162	0.903	0.050	0.361	0.587	0.638	1.756	0.62
		14	0.121	262.9	194.5	0.220	0.076	0.202	1.406	0.197	0.311	0.818	0.842	2.531	1.79
		15	0.072	361.4	715.2	0.453	0.110	1.155	2.196	0.515	1.177	3.338	3.614	5.665	6.53
		16	0.189	544.8	510.1	0.125	0.012	0.316	2.930	0.128	0.450	1.281	1.088	0.886	6.85

Table 3-4. Continued

River		Site #	Hg	Al	Fe	As	Pb	Cu	Mn	Co	Ni	V	Cr	Zn	% OM
Upper Pra		17	0.079	226.8	432.9	0.180	0.060	0.386	4.883	0.112	0.356	3.378	1.176	1.526	1.91
		18	0.678	158.1	166.2	0.079	0.214	0.169	2.658	0.023	0.300	0.594	0.620	0.802	2.89
		19	0.071	273.7	376.1	0.115	0.014	0.323	5.002	0.249	0.441	1.252	1.273	1.201	1.56
		20	0.180	736.9	1266.3	0.133	0.160	1.010	10.704	0.517	0.874	0.861	2.401	1.603	7.91
		21	0.070	236.8	290.2	0.165	2.441	0.299	3.546	0.138	0.342	0.834	1.100	1.286	3.47

Table 3-5: Total metal concentrations in mg/kg dry weight (ppm) and organic matter content determined as loss on ignition (LOI) on river sediments collected from the Pra River basin during "January 2003 dry season".

River		Site #	Hg	Al	Fe	As	Pb	Cu	Mn	Co	Ni	V	Cr	Zn	% OM
Section															
Lower		1	0.003	90.0	141.0	0.216	<0.003	0.018	3.031	<0.001	0.252	0.204	0.203	0.569	0.46
Pra		2	0.008	308.0	214.0	0.146	<0.003	0.089	2.828	<0.001	0.400	0.484	0.523	1.199	3.15
		3	0.002	406.0	236.0	0.281	<0.003	0.153	5.102	<0.001	0.457	0.645	0.732	0.704	1.68
		4	0.017	570.0	283.0	0.355	<0.003	0.207	4.461	<0.001	0.457	0.878	0.985	1.280	4.74
		5	0.005	117.0	68.0	0.218	<0.003	0.029	1.470	<0.001	0.301	0.145	0.267	0.746	0.25
		6	0.043	198.0	271.0	0.370	<0.003	0.192	7.890	<0.001	0.453	0.619	0.579	1.152	0.96
		7	0.009	287.0	135.0	0.158	<0.003	0.091	2.573	<0.001	0.343	0.475	0.575	0.557	0.00
		8	0.002	245.0	247.0	0.458	<0.003	0.133	8.221	<0.001	0.574	0.548	0.537	0.756	3.01
Offin		9	0.008	315.0	202.0	0.230	<0.003	0.153	4.140	<0.001	0.450	0.525	0.964	1.004	0.46
		10	0.007	320.0	189.0	0.181	<0.003	0.105	5.825	<0.001	0.428	0.528	0.516	0.964	0.40
		11	0.118	660.0	393.0	5.076	<0.003	1.112	7.034	<0.001	1.015	1.326	1.305	1.274	0.47
		12	0.026	323.0	178.0	0.940	<0.003	0.185	3.157	<0.001	0.542	0.606	0.588	1.065	2.48
		13	0.007	462.0	219.0	0.759	<0.003	0.257	3.850	<0.001	0.554	0.794	0.831	0.819	0.53
		14	0.018	1449.0	1077.0	0.613	<0.003	0.992	5.609	<0.001	1.088	3.750	4.322	2.013	0.47
		15	0.036	699.0	1228	0.235	<0.003	0.574	7.904	<0.001	1.058	3.082	2.756	1.833	2.79
		16	0.010	420.0	248.0	0.139	<0.003	0.134	5.241	<0.001	0.511	0.621	0.781	0.933	4.39

Table 3-5. Continued

River		Site #	Hg	Al	Fe	As	Pb	Cu	Mn	Co	Ni	V	Cr	Zn	% OM
Section															
Upper		17	0.002	407.0	497.0	0.125	<0.003	0.150	5.016	<0.001	0.437	0.867	1.030	1.027	1.74
Pra		18	0.002	318.0	116.0	0.088	<0.003	0.072	2.195	<0.001	0.429	0.461	0.522	0.728	0.52
		19	0.005	509.0	356.0	0.124	<0.003	0.196	9.781	<0.001	0.568	0.885	1.031	1.171	0.39
		20	0.030	288.0	378.0	0.103	<0.003	0.261	4.480	<0.001	0.429	1.219	1.755	0.666	0.84
		21	0.043	247.0	243.0	0.369	<0.003	0.049	2.495	<0.001	0.569	0.349	0.333	0.881	2.91

Table 3-6: Pearson correlation coefficients for sediment data collected during the dry season. Lead (Pb) and cobalt (Co) are not included as their concentrations were below instrument analytical detection in samples collected in January 2003 dry season

	Hg	Al	Fe	As	Cu	Mn	Ni	V	Cr	Zn	%OM
Hg	1.000										
Al	0.226	1.000									
Fe	0.231	0.783*	1.000								
As	0.864*	0.255	0.069	1.000							
Cu	0.691**	0.809*	0.681	0.716**	1.000						
Mn	0.252	0.330	0.461	0.209	0.405	1.000					
Ni	0.579**	0.817*	0.825*	0.526	0.899*	0.504	1.000				
V	0.257	0.894*	0.958*	0.149	0.783*	0.397	0.858*	1.000			
Cr	0.199	0.908*	0.906*	0.107	0.764*	0.340	0.793*	0.978*	1.000		
Zn	0.328	0.822*	0.842*	0.204	0.710**	0.449	0.814*	0.848*	0.797*	1.000	
%OM	-0.034	0.008	0.091	-0.148	-0.150	0.054	0.057	-0.007	-0.064	0.195	1.000

\*  $p < 0.01$ ; \*\*  $p < 0.05$

Table 3-7: Pearson Correlation coefficients for sediment data collected during the June 2002 wet season.

	Hg	Al	Fe	As	Pb	Cu	Mn	Co	Ni	V	Cr	Zn	%OM
Hg	1.000												
Al	-0.069	1.000											
Fe	-0.119	0.896*	1.000										
As	-0.003	0.058	-0.023	1.000									
Pb	-0.020	-0.040	-0.013	-0.107	1.000								
Cu	-0.042	0.660*	0.801*	0.414	-0.024	1.000							
Mn	-0.137	0.476	0.523	-0.169	-0.026	0.167	1.000						
Co	-0.100	0.622**	0.749*	0.191	-0.092	0.819*	0.204	1.000					
Ni	-0.163	0.640**	0.803*	0.083	-0.074	0.899*	0.229	0.834*	1.000				
V	-0.099	0.241	0.423	0.071	-0.066	0.586**	-0.006	0.408	0.582	1.000			
Cr	-0.096	0.629	0.796*	0.081	0.028	0.908*	0.220	0.815*	0.971*	0.690**	1.000		
Zn	-0.082	0.029	0.117	0.488	-0.132	0.508**	-0.462	0.610	0.445	0.334	0.399	1.000	
%OM	0.432	0.415	0.330	-0.095	-0.014	0.243	0.296	0.162	0.277	0.034	0.275	-0.224	1

\* $p < 0.01$ ; \*\* $p = 0.05$ .

### 3.4.4 Assessment of the Contamination Level of Pra River Sediments

Variability in trace metal concentrations in sediments could be driven by natural and/or anthropogenic sources, and in sediment matrices, metals are usually associated chiefly with the fine-grained sediment fractions. There is no generally accepted protocol for selecting a sediment constituent to be used for normalization, and several approaches/elements have been used ranging from simple metal/normalizer ratios (Singh et al., 1997; Datta and Subramanian, 1998; Birch et al., 2001) to more complex methods based on regression analyses (e.g. Rowlatt and Lovell, 1994). Metal to normalizer ratio approaches include the determination of the enrichment factor (EF) (e.g., Sutherland, 2000) and the geo-accumulation index (Igeo), which was originally proposed by Muller (1969). In normalization approaches, the background concentrations used are usually values reported for shale or the earth's upper crust. But, in few specific cases, use of local background values, when available, seems more appropriate, particularly when the latter is orders of magnitude lower than the shale and/or the crust reference values (e.g. Ram et al., 2003; Woitke et al. 2003). In spite of the above, prominent among them are aluminum, iron, lithium, total organic carbon and grain size (e.g. Windom et al., 1989; Loring, 1990; Loring and Rantala, 1992; Daskalakis and O'Connor, 1995; Aloupi and Angelidis, 2001a, 2001b). Based on published information, it is apparent that Al has been the most commonly used tracer element in normalization calculations/models. Several reasons explain the choice of Al over others. It is a major component of fine-grained aluminosilicate minerals. As an essential component of these smallest sized particles, Al is a good surrogate for clay particles (Windom et al., 1989; Daskalakis and O'Connor, 1995), which constitute the bulk of adsorption sites for metals on sediment

particles. In contrast, use of organic carbon content as a normalizer has shown weaker correlations than Al (Windom et al., 1989; Horowitz, 1991). Iron is not as a good matrix element as Al because it is chemically active in both oxic and anoxic environments, hence is always associated with surfaces (Daskalakis and O'Connor, 1995). Based on these observations, Al was chosen as normalizer in this study. Additionally, using the reported background shale values for Hg and other metals of interest (refer Turekian and Wedepohl, 1961; Mason and Chapman, 1982), the sediment enrichment factor (EF) was calculated using THg, other total metals and Al data obtained from the <63µm sediment fraction (Subramanian and Mohanachandra, 1990; Sahu and Bhosale, 1991; Rodrigues-Filho and Maddock, 1997). The following equation was used to determine the enrichment factor (EF) calculated as:

$$EF = \frac{\left(\frac{Me}{Al}\right)_{sample}}{\left(\frac{Me}{Al}\right)_{background}}$$

where Me and Al are the concentrations of the metal of interest in the sample and at the same time, the reference for background concentrations. Thus, to assess deviation of measured THg concentrations in sediments from background values as well as the impact of AGM on levels of other heavy metals investigated in this study, Hg and metals of interest were co-varied with Al to determine the level of sediment contamination that is the concentration above what would naturally occur. In this study, shale reference values taken from Turekian and Wedepoll (1961) were used, and the calculated EF values for each of the analyzed metals are presented in Table 3-8 (wet season) and 3-9 (dry season).



#### **3.4.4.1 Mercury enrichment in the sediments**

The range of EF values obtained during the rainy season is indicative of contamination, with extremely severe contamination at two of the 21 sites, whereas EF values obtained in the dry season show much cleaner sediments, Tables 3-8 and 3-9. Figure 3-5 shows the differences between the two seasons, with the rainy season plotting above the dry season. Therefore, by the EF approach, it appears that riverine sediments in the Pra River system receive high loads of Hg on a cyclic basis, and these inputs temporally increase THg levels above background concentrations (i.e., higher inputs of Hg-contaminated particles in the rainy season). In the dry season however, contamination is reduced, and lower EF values are obtained as fine Hg-contaminated particles are transported downstream and probably discharged into the Gulf of Guinea, the terminal basin for the Pra River. If true, this could then have long-term implications with regard to the local fishing industry since the Gulf of Guinea serves as an important fishing site for both local inhabitants and commercial fishing.

Table 3-8. Calculated enrichment factors\* (EF) for analyzed elements in sediment samples collected in the June 2002 rainy season. Shale reference values were taken from Turekian and Wedepohl (1961).

River	Section	Site #	Hg	Fe	As	Pb	Cu	Mn	Co	Ni	V	Cr	Zn
Lower	Pra	1	47	2	9	3	2	2	1	2	2	3	4
		2	57	2	9	1	2	3	2	2	2	3	5
		3	2463	1	6	3	2	1	2	1	2	3	6
		4	25	2	8	2	2	2	2	2	2	3	4
		5	53	2	13	2	2	4	5	2	3	4	6
		6	106	1	12	1	1	2	2	2	2	3	3
		7	20	2	13	0	2	3	3	2	2	3	4
		8	178	2	12	1	2	2	3	2	2	3	3
Offin		9	37	2	4	1	2	1	8	3	2	3	29
		10	79	3	43	5	5	3	5	5	4	6	25
		11	111	1	19	0	2	0	4	2	2	3	15
		12	207	2	84	0	5	0	4	2	2	4	15
		13	36	1	3	3	2	0	1	2	2	3	8
		14	92	1	5	1	1	1	3	1	2	3	8
		15	40	3	8	1	6	1	6	4	6	9	13
		16	69	2	1	0	1	1	1	1	1	2	1

Table 3-8. Continued

River		Section	Site #	Hg	Fe	As	Pb	Cu	Mn	Co	Ni	V	Cr	Zn
Upper Pra		Upper	17	70	3	5	1	3	2	2	2	9	5	6
		Pra	18	858	2	3	5	2	2	1	2	2	3	4
			19	52	2	3	0	2	2	4	2	3	4	4
			20	49	3	1	1	2	1	3	1	1	3	2
			21	59	2	4	41	2	1	2	2	2	4	5

*EF defined as: EF<2 deficient to minimal enrichment; EF=2-5 moderate enrichment; EF=5-20 significant enrichment; EF=20-40 very high enrichment; and EF>40 extremely high enrichment (Loska et al., 2004).*

Table 3-9. Calculated enrichment factors (EF) for analyzed elements in sediment samples collected during the January 2003 dry season. Shale reference values were taken from Turekian and Wedepohl (1961). \*ND = not detected

River		Site #	Hg	Fe	As	Pb	Cu	Mn	Co	Ni	V	Cr	Zn
Lower	Pra	1	7	3	15	*ND	0	3	ND	3	1	2	5
		2	5	1	3	ND	1	1	ND	2	1	2	1
		3	1	1	4	ND	1	1	ND	1	1	2	2
		4	6	1	4	ND	1	1	ND	1	1	2	3
		5	9	1	11	ND	0	1	ND	3	1	2	5
		6	43	2	11	ND	2	4	ND	3	2	3	5
		7	6	1	3	ND	1	1	ND	1	1	2	2
		8	2	2	12	ND	1	3	ND	3	1	2	3
Offin		9	5	1	4	ND	1	1	ND	2	1	3	3
		10	4	1	3	ND	1	2	ND	2	1	1	3
		11	36	1	47	ND	3	1	ND	2	1	2	2
		12	16	1	18	ND	1	1	ND	2	1	2	3
		13	3	1	10	ND	1	1	ND	1	1	2	1
		14	2	1	3	ND	1	0	ND	1	2	3	1
		15	10	3	2	ND	1	1	ND	2	3	4	2
		16	5	1	2	ND	1	1	ND	1	1	2	2

Table 3-9. Continued

River		Section	Site #	Hg	Fe	As	Pb	Cu	Mn	Co	Ni	V	Cr	Zn
Upper Pra			17	1	2	2	ND	1	1	ND	1	1	2	2
			18	1	1	2	ND	0	1	ND	2	1	1	2
			19	2	1	1	ND	1	2	ND	1	1	2	2
			20	21	2	2	ND	2	1	ND	2	3	5	2
			21	35	2	9	ND	0	1	ND	3	1	1	3

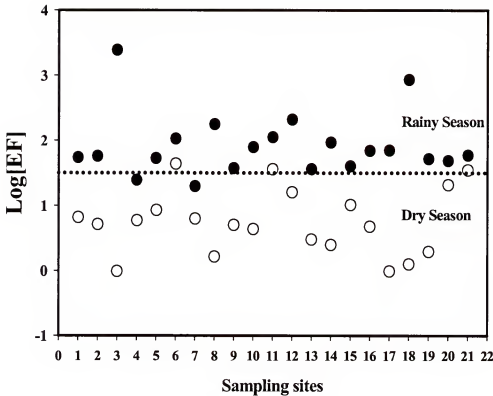


Figure 3-5. Trends of the enrichment factor (EF) in the rainy (full circles) and dry (empty circles) seasons. The dotted horizontal line shows the point of quasi separation of rainy and dry seasons.

#### 3.4.4.2 Co-variation of mercury and other metals with Al

Scatter plots of metals versus normalizer (Al) were used to decipher anthropogenic impacts on concentrations of metals of interest. The regression of each metal on Al in the natural sediment was calculated using data from Table 3-4 and 3-5, and possible contaminated sites were identified using previously published procedures (refer Loring, 1991; Loring and Rantala, 1992; Aloupi and Angelidis, 2001a, b). All points within the 95% confidence band were classified as natural or background levels, while points beyond the 95% confidence interval were considered impacted by human activities. The graphs produced using this approach is presented in Figures 3-6 through 3-16.

**3.4.4.2.1 Mercury (Hg), Arsenic (As), Lead (Pb) and Zinc (Zn).** Hg and As (in both the wet and dry seasons), and Pb and Zn (in the dry season only) gave a rather similar distribution when plotted against Al concentrations (Figures 3-6, 3-7, 3-8, and 3-9). All outliers on these plots corresponded to samples from sites directly impacted by

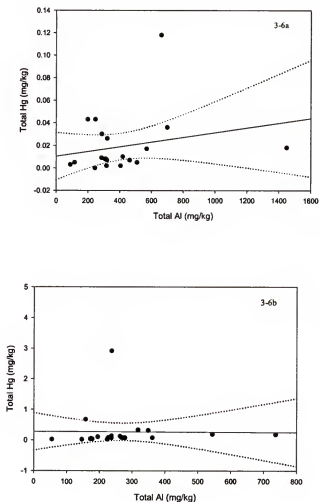


Figure 3-6. Hg: Al scatter plot for sediments of the Pra River basin: 3-6a = dry season and 3-6b = rainy season. The dotted lines represent the 95% confidence interval.

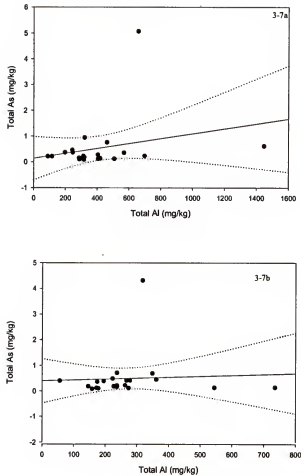


Figure 3-7. As: Al scatter plot for sediments of the Pra River basin: 3-7a = dry season and 3-7b = rainy season. The dotted lines represent the 95% confidence interval mining centers. Although most data points in these graphs fell within the 95% confidence interval, the observed lack of relationships was likely an indication of anthropogenic impact on initially very low concentrations. This observation was validated by the calculated enrichment factors (EF) for each of the analyzed metals



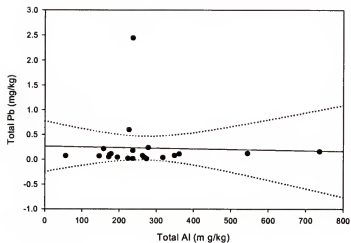


Figure 3-8. Pb:Al scatter plot for sediments of the Pra River basin: rainy season. The dotted lines represent the 95% confidence interval.

presented in Table 3-8 (wet season) and 3-9 (dry season). It was obvious that Zn, Hg and As were the only elements to show high enrichment above background. These data supported the suggestion that the increase in Zn and As concentrations above empirical background values in this river system was primarily driven by AGM activities. This observation was substantiated by the positive relationships between Hg and both As and Zn during the dry season. However, while Hg and As concentrations were significantly and positively correlated in the dry season ( $r = 0.864$ ;  $P < 0.001$ ), this relationship fell apart in the wet season ( $r = -0.003$ ) (Tables 3-8 and 3-9b). Hg showed only a weak but significant relationship with Zn ( $r = 0.328$ ;  $p < 0.001$ ) during the dry season. On the other hand, and despite its similar distribution to that of Hg along the Al gradient, Pb (detected in samples collected in the wet season only, Figure 3-8) did not correlate with Hg ( $r = -0.02$ ). Since Hg was the only element with a well known input source for the system

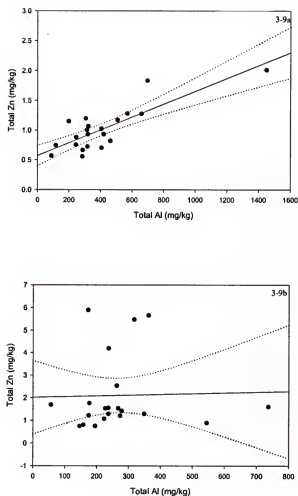


Figure 3-9. Zn: Al scatter plot for sediments of the Pra River basin: 3-9a = dry season and 3-9b = rainy season. The dotted lines represent the 95% confidence interval.

under study, its correlation with As and Zn in the dry season suggests that the levels of both As and Zn were somewhat impacted by AGM in the Pra River basin. However, the lack of correlation between Hg and any of the metals in the rainy season showed the importance of changes in hydrologic conditions on levels and the fate of trace metals in aquatic systems. One probable explanation was that the increase in run-off and Hg-contaminated particles input into the river during the rainy season affected the Hg:Metal ratio and favors the highly particle reactive Hg. It is therefore suggested that Hg inputs

from mining contaminated soils/tailings occur mostly during the rainy season via soil erosion and storm water runoff.

**3.4.4.2.2 Iron (Fe) and Manganese (Mn).** The naturally abundant metals Fe and Mn whose concentrations in the sediments are normally not greatly affected by AGM, co-varied with Al (Figure 3-10 and Figure 3-11), with Fe showing stronger relationships with Al, regardless of the season. Mn showed much weaker relationships with Al and signs of anthropogenic impacts were illustrated by a much higher number of outliers in Figure 3-11a and 3-11b as compared to Fe, which showed a positive and significant relationship with Al in both the rainy and dry seasons (Table 3-6 and 3-7). This was further substantiated by the EF values Table 3-8 and 3-9, with few sites showing moderate enrichment particularly in the rainy period. One possibility could be the introduction of Mn into waterways by erosion/runoff following exposure and oxidation of reduced minerals.

**3.4.3.2.3 Copper (Cu), Nickel (Ni), Chromium (Cr), Cobalt (Co), and Vanadium (V).** These elements (Figures 3-12 to 3-16) gave good and significant relationships with aluminum (Table 3-6 and 3-7), suggesting that with the exception of a very few outliers, the determined levels corresponded to values at or near background concentrations. Overall, the relationship between any of the metals and Al was stronger during the dry season and tended to be less so in the wet season. Also, most of these elements showed positive and significant relationships with Zn (Table 3-6 and 3-7), but no relationship with Hg. It is likely that some of these elements are associated primarily with sulfide minerals of Zn and are of natural origin.

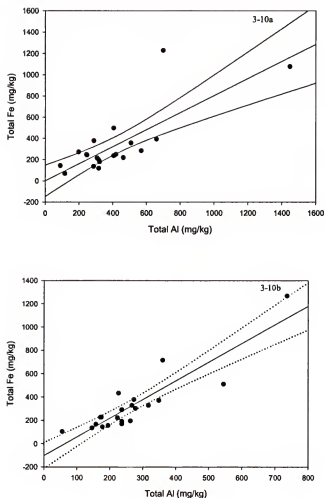


Figure 3-10. Fe: Al scatter plot for sediments of the Pra River basin: 3-10a = dry season and 3-10b = rainy season. The dotted lines represent the 95% confidence interval.

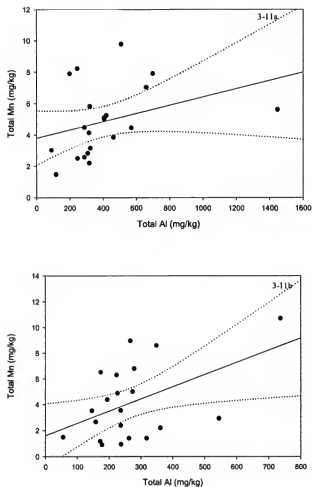


Figure 3-11. Mn: Al scatter plot for sediments of the Pra River basin: 3-11a = dry season and 3-11b = rainy season. The dotted lines represent the 95% confidence interval.

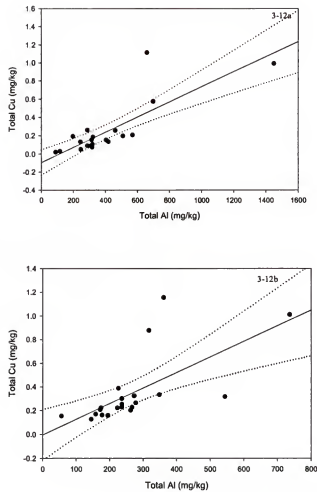


Figure 3-12. Cu: Al scatter plot for sediments of the Pra River basin: 3-12a = dry season and 3-12b = rainy season. The dotted lines represent the 95% confidence interval.

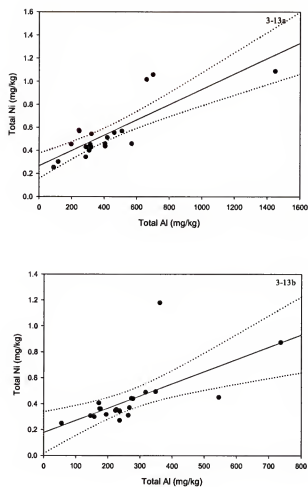


Figure 3-13. Ni: Al scatter plot for sediments of the Pra River basin: 3-13a = dry season and 3-13b = rainy season. The dotted lines represent the 95% confidence interval.

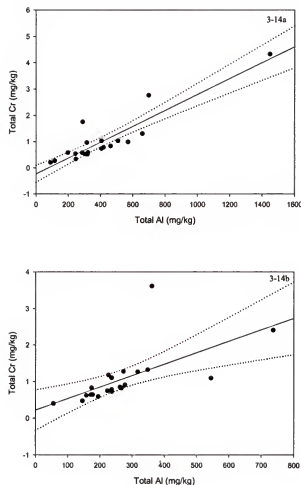


Figure 3-14. Cr: Al scatter plot for sediments of the Pra River basin: 3-14a = dry season and 3-14b = rainy season. The dotted lines represent the 95% confidence interval.



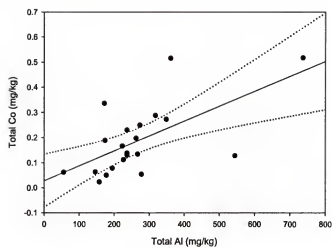


Figure 3-15. Co: Al scatter plot for sediments of the Pra River basin: rainy season. The dotted lines represent the 95% confidence interval.

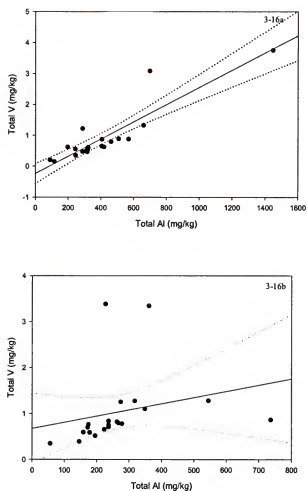


Figure 3-16. V: Al scatter plot for sediments of the Pra River basin: 3-16a = dry season and 3-16b = rainy season. The dotted lines represent the 95% confidence interval.

### 3.4.5. Mercury in Soils

Soil samples were obtained from locations near sites of water and sediment sample collection (Figure 3-2). At sites 9, 12, 13, 14, and 15, additional soil samples were collected along outward transects from mining centers in the wet season only. Measured THg and MeHg concentrations, as well as the organic matter content of these soil samples, are presented in Table 3-10. Besides the three peak values obtained in samples collected from sites #7 ( $4.87 \text{ mg Kg}^{-1}$ ) and # 13 ( $5.55 \text{ mg Kg}^{-1}$ ) in the rainy season, and site #6 ( $1.1 \text{ mg Kg}^{-1}$ ) in the dry season, no marked differences were observed in THg levels from mining versus non-mining sites. Hg was detected in both the wet and dry seasons without major changes in concentration trends. However, MeHg was undetectable in soil samples collected in the dry season, and this was likely due to the low water content of these dry soils, which could be the limiting factor for microbial driven MeHg production when compared with the nearly wet at field capacity soil samples collected in the rainy season. Further, MeHg levels observed in the soils followed almost a similar trend as observed in the aqueous phase (Table 3-2), as higher values were recorded during the high flow period, and lower concentrations including several values below the analytical detection limit were found in the dry period. Although no statistically significant relationship was observed between the two parameters, the striking similarity in MeHg trends in the two compartments presupposed a non-linear linkage between the two. As hypothesized earlier, these trends suggested that terrestrial sources could account for a good portion of MeHg found in the river channel. As a consequence, the potential of both soils and sediments to produce MeHg versus seasons

Table 3-10. Total and methyl-Hg concentrations in mg/kg and percent Organic Matter (% OM) in soil samples collected during June 2002 rainy and January 2003 dry periods.

Pra River sections	System Sites number	Site characteristics	THg		MeHg		%OM	
			Wet Season	Dry Season	Wet Season	Dry Season	Wet Season	Dry Season
Lower Pra	1	Non-Mining	0.008	0.012	0.003	<0.001	0.75	0.36
	2	Non-mining	0.042	0.010	0.010	<0.001	4.27	1.01
	3	Non-mining	0.011	0.007	0.005	<0.001	0.50	0.51
	4	Non-mining	0.027	0.015	0.007	<0.001	2.08	1.05
	5	Mining site	0.011	0.006	0.004	<0.001	0.86	0.37
	6	Non-mining	0.260	1.106	0.048	<0.001	4.38	2.30
	7	Past-mining	4.876	<i>nd</i>	0.128	<i>nd</i>	1.78	<i>nd</i>
	8	Mining site	0.089	0.015	0.030	<0.001	0.90	2.09
Offin		Tailings impacted	0.015	0.010	0.004	<0.001	0.45	0.47
		Amalgamation	0.052	<i>nd</i>	0.008	<i>nd</i>	1.59	<i>nd</i>
	9	*100m	0.066	<i>nd</i>	0.034	<i>nd</i>	4.51	<i>nd</i>
		*500m	0.140	<i>nd</i>	0.008	<i>nd</i>	6.04	<i>nd</i>
	10	Mining	0.036	0.028	0.020	<0.001	2.24	17.56
		Tailings impacted	0.025	<i>nd</i>	0.015	<i>nd</i>	0.17	<i>nd</i>
	11	Mining site	0.034	0.023	0.016	<0.001	0.49	0.38
	12	Mining site	0.057	0.016	0.004	<0.001	1.58	0.65
		*100 m	0.543	<i>nd</i>	0.141	<i>nd</i>	1.22	<i>nd</i>
		*300m	0.062	<i>nd</i>	0.020	<i>nd</i>	2.92	<i>nd</i>
		*500m	0.022	<i>nd</i>	0.010	<i>nd</i>	1.11	<i>nd</i>
	13	Mining site	<i>nd</i>	0.028	<i>nd</i>	<0.001	<i>nd</i>	0.56
		Roasting site	5.547	<i>nd</i>	0.162	<i>nd</i>	1.32	<i>nd</i>
		*100m	0.168	<i>nd</i>	0.003	<i>nd</i>	0.23	<i>nd</i>
		*300m	0.060	<i>nd</i>	0.005	<i>nd</i>	1.34	<i>nd</i>
		*500m	0.015	<i>nd</i>	0.010	<i>nd</i>	4.18	<i>nd</i>
	14	Mining site	0.272	0.022	0.008	<0.001	9.92	0.37
		*300m	0.036	<i>nd</i>	0.005	<i>nd</i>	0.56	<i>nd</i>
		*500m	0.074	<i>nd</i>	0.002	<i>nd</i>	1.82	<i>nd</i>

Table 3-10. Continued

Pra River sections	System Sites	Site characteristics	THg		MeHg		%OM	
			Wet Season	Dry Season	Wet Season	Dry Season	Wet Season	Dry Season
Upper Pra/Birim	15	Tailings impacted	0.029	0.025	0.002	<0.001	3.86	nd
		Roasting site	0.052	nd	0.013	nd	1.89	5.42
		*100m	0.028	nd	0.010	nd	1.26	nd
		*300m	0.070	nd	0.028	nd	2.92	nd
		*500m	0.027	nd	0.020	nd	5.41	nd
	16	Non-mining	0.149	0.031	0.054	<0.001	1.47	2.10
	17	Non-mining	0.197	0.012	0.042	<0.001	3.06	2.15
	18	Mining site	0.138	0.010	0.050	<0.001	1.97	0.65
	19	Mining site	0.079	0.031	0.030	<0.001	4.94	5.11
	20	Mining site	0.093	0.037	0.020	<0.001	1.54	2.88
	21	Mining site	0.091	0.009	0.018	<0.001	1.90	1.11

is considered in a laboratory study, which is discussed in chapter 4. Finally, the investigation of the distribution of Hg concentrations away from points of different mining activities in the rainy season (Table 3-10) showed no consistent increasing or decreasing trends, and overall, mean THg soil values from the Pra River were lower than those reported for river systems used for comparison in earlier sections, 3-4.1 and 3-4.2. In all, the highest THg values were from the active AGM areas, and the maxima exceeding the  $0.2 \text{ mg Kg}^{-1}$  limit of USEPA were from sites #13 and #7 (Table 3-10 and Figure 3-2). Finally, soil mean values in the Pra basin in both seasons ( $0.365 \text{ mg Kg}^{-1}$  (wet) and  $0.073 \text{ mg Kg}^{-1}$  (dry)) were lower than the average value ( $0.390 \text{ mg Kg}^{-1}$ ) found along the well studied Madeira River in the Brazilian Amazon.

### 3.4.6 Mercury in Biological Tissues

#### 3.4.6.1. Mercury in Fish Tissues

Due to limited fish availability, only a total of 12 fishes were purchased from fishermen in villages along the Pra River. As a result, the data presented here simply illustrate the average concentrations of Hg versus the fish trophic levels (Table 3-11). Two bottom feeders (*Claria sp* and *Synodontis, sp*) and the piscivorous fish (*Hepsetus odoe*) had average THg concentrations above the WHO's safe consumption guideline of  $0.5 \text{ mg Kg}^{-1}$ . In contrast, tilapia (*Sarotherodon melantheron*) showed THg concentrations below the above-mentioned guideline. Curiously, and unlike in most reports on Hg fish data determined on fish tissues, the fraction of THg occurring as MeHg represented <1% in all fish samples analyzed in this study. Efficient recoveries on tested reference material (DORM-2) described in the analytical section of this chapter suggest that this is not an analytical problem. However, the technique of fish dehydration via smoking used by villagers for long-term conservation purposes could explain the observed low MeHg. One could speculate that heat-driven MeHg degradation during the smoking process is responsible for the observed low MeHg values. However, since no fresh fish tissues were analyzed in this study, it is therefore impossible to conclude without reservation on the

Table 3-11. Average total and methyl-Hg concentrations in tissues (dry weight) from four different fish species that are common in local people's diet collected along Pra River during January 2003 dry season.

Species Scientific Name	Common Name	Diet habit	n	Average weight (g)	Average length	Average THg	Average MeHg mg/kg
<i>Synodontis sp</i>	Cat fish	Bottom feeder	4	17.58±16.48	14.45±8.94	0.69±0.57	0.0035±0.0012
<i>Hepsetus Odoe</i>	Kafue pike	Piscivorous	2	66.01±1.41	26.0±1.41	4.473±0.42	0.0072±0.0014
<i>Clarias sp</i>	Mud fish	Bottom feeder	2	40.60±28.43	22.25±6.72	1.04±0.05	0.0019±0.0001
<i>Sarotherodon melantheron</i>	Tilapia	Planktivorous	4	22.75±8.19	15±1.58	0.08±0.01	<0.001

cause of the observed low MeHg levels. Since smoked fish is the main form of fish consumed predominantly during the long rainy season, the smoking practice might reduce exposure to significant amounts of MeHg. It is clear that a more comprehensive investigation of Hg in fish tissues (dry and fresh) encompassing spatial and temporal variations and more trophic levels is needed

### **3.4.6.2 Mercury in Human Hair**

As stated earlier, hair samples came from 53 subjects in the rainy period from a total of 9 sites (Table 3-12) and only 7 individuals volunteered in the dry season, all from site #6 (Table 3-13). Miners contributed the majority of obtained hair samples. The highest THg levels were found in the dry season (Table 3-13); likewise MeHg. Overall, high levels of Hg were observed in active mining areas (upper river reaches) (sites # 5, 6, 9, 11, 12 and 14) than the non mining centers (lower reaches) (sites # 1, 2, 3, and 4). With reference to age and THg, no significant relation was found ( $r^2 = 0.02$ ;  $p > 0.05$ ) particularly in the rainy period. Thus, THg concentrations in the hairs of adults and young hairs did not indicate any consistent trends. The females on the other hand, were small in number (two) nevertheless the hair Hg value observed in the two donors was lower than many of the hair Hg in the male counterparts. In all the cases examined, the miners were greatly exposed to Hg than professionals with reference to THg (Tables 3-12 and 3-13). In general, the proportion of MeHg in head hair to THg in individuals was below 50% of the THg with the exception of few individuals among the reverine population downstream (sites # 3 and 4, Table 3-12), indicating that inorganic Hg was the predominant form of Hg in the hair samples. Most miners interviewed confessed to eating fish at least four times a week. As such Hg exposure for these miners is likely due to both direct exposures to Hg vapor during the gold extraction processes and ingestion of Hg-



contaminated fish. The probable route for the riparian population downstream to Hg exposure is through the intake of Hg contaminated fish; which is the result of gold extraction and recovery processes by amalgamation leading to excessive leaching and

Table 3-12. THg and MeHg concentrations in mg/kg in head hair samples collected from indigenous people along the Pra River during the rainy period of June 2002. Samples were collected from villages corresponding to the listed site numbers. The number of individuals per site is listed in column 2.

Sampling site #	n	Age	Sex	Occupation	THg	MeHg
1	5	43	M	Farming	1.58	0.11
		20	M	Student	0.40	0.11
		17	M	Student	0.41	<0.01
		45	M	Fishing	1.66	0.03
		50	M	Farming	4.13	0.12
2	5	46	M	Farming	0.77	0.19
		21	M	Farming	1.19	0.10
		55	M	Storekeeper	0.39	<0.01
		32	M	Farming	1.02	0.20
		35	M	Farming	0.48	0.06
3	2	22	M	Trader	1.37	0.59
		15	M	Farming	0.43	0.03
4	10	18	M	Unemployed	1.16	0.89
		25	F	Trader	0.71	0.07
		27	M	Mechanic	0.69	<0.01
		60	M	Farming	1.29	0.83
		26	F	Housewife	0.63	0.37
		22	M	Laborer	1.00	0.32
		40	M	Sanitary job	0.85	0.07
		23	M	Unemployed	0.85	0.07
		27	M	Farming	0.97	0.04
		32	M	Farming	1.56	0.36

Table 3-12. Continued

Sampling site #	n	Age	Sex	Occupation	THg	MeHg
5	2	24	M	Farming	0.54	0.12
		26	M	Farming	0.55	0.17
9	7	32	M	Mining	0.87	0.13
		55	M	Mining	0.60	0.10
		22	M	Mining	0.70	0.13
		29	M	Mining	1.09	0.08
		36	M	Mining	0.93	0.23
		30	M	Mining	0.82	0.44
		32	M	Mining	0.58	0.06
11	4	26	M	Mining	0.79	<0.01
		30	M	Mining	1.39	0.25
		27	M	Mining	1.83	0.06
		29	M	Mining	1.38	0.22
12	8	15	M	Mining	0.99	<0.01
		47	M	Mining	0.96	0.33
		25	M	Mining	0.69	0.01
		28	M	Mining	1.12	<0.01
		12	M	Mining	0.85	<0.01
		28	M	Mining	0.96	0.01
		16	M	Mining	2.73	0.07
		38	M	Mining	1.44	<0.01
		29	M	Mining	2.41	0.21
		15	M	Mining	0.68	<0.01
14	12	22	M	Mining	1.27	<0.01
		40	M	Mining	1.42	0.07
		32	M	Mining	1.50	0.20
		20	M	Mining	0.75	<0.01
		20	M	Mining	0.98	0.19
		19	M	Mining	1.81	0.40
		39	M	Mining	1.22	0.25
		25	M	Mining	1.34	<0.01
		22	M	Mining	1.41	0.19
		34	M	Mining	1.17	0.02

Table 3-13. THg and MeHg concentrations in mg/kg in head hair samples collected from indigenous people at the sampling location number 6 during the dry period of January 2003.

Sampling Site	<i>n</i>	Age	Sex	Occupation	THg	MeHg
6	7	23	M	Mining	3.42	0.138
		34	M	Mining	6.50	0.278
		36	M	Mining	2.65	<0.01
		39	M	Mining	5.26	0.060
		33	M	Mining	0.89	0.211
		33	M	Mining	2.19	<0.01
		33	M	Mining	1.51	0.661

dispersing of Hg to reach non-mining areas downstream. The consequence is the accumulation of Hg in aquatic organisms as evidenced in the most utilized fish species (Table 3-11). In addition, differences in number of head hair in the two seasons was large (Tables 3-12 and 3-13), yet the mean Hg concentration in hair does confirm other findings elsewhere that, the dry period is always richer in Hg than the wet. As most often seen there is less consumption of fish and gold mining in the high water period.

In spite of this, Hg levels measured in hair samples obtained from both miners and non-miners were on the low end and far below the 50mg Kg-1 guideline recommended by the World Health Organization (WHO, 1976). In general, average Hg values measured in Ghanaian hair samples were much lower than those documented in the literature for Brazil (8.89 mg Kg-1, Madeira River and 16.2 mg Kg-1, Tapajós River) and the Philippines 4.14 mg Kg-1), two countries where similar mining operations prevail. These trends could be explained partly by differences in dietary habits in these locations during the time of sample collection. Nevertheless, the findings of Hg in hair from Ghana do confirm seasonal variations of previous studies carried out in the Brazilian Amazon

(Akagi et al., 1995; Kehrig et al., 1997; Dolbec et al., 2001; Maurice-Bourgoin et al., 2003; Coquery et al., 2003), where high levels of Hg in hair in the dry period were linked to the consumption of fish abundant at that time, unlike the wet period (Malm et al., 1995; Barbosa et al., 1995; Bidone et al., 1997) characterized by minimal fish catch.

### 3.5 Conclusions

Besides the obvious Hg point sources along the Pra and its tributaries, the obtained results show that Hg levels and speciation in the studied aquatic system are controlled by precipitation, which drives hydrology and differences in flow regimes versus seasons. The seasonal difference in Hg speciation suggests that MeHg found in the aqueous phase and riverine sediments is predominantly of terrestrial origin, where its production is favored during the rainy season by high soil water content. This hypothesis has been tested and is the subject of Chapter 4. Use of the enrichment factor (EF) for assessment of sediment quality indicated moderate to severe contamination of surface sediments in the rainy season, while in the dry season, it indicated nearly no pollution of surface sediments with reference to Hg. Accordingly, most of the Hg introduced into this river system is likely transported to depositional downstream terminal basins (e.g. the river delta and the Gulf of Guinea). With regard to biota, Hg measured in hair in the dry period was higher than data obtained on samples collected during the wet period. This could be explained in part by the shift in diet as a result of abundance of fish in the local markets and the concurrent increase and more active fishing during the dry season. Mercury data obtained on a very limited number of fish samples collected during the dry period showed low MeHg levels that could be the result of the smoked fish used leading to MeHg degradation. On the other hand, concentrations of Fe, Cu, Mn, Co Ni, V, Cr and Zn co-varied with Al, suggesting that natural sources accounted for the observed levels. Only

As and Zn were significantly correlated to THg in the dry season, implying that the increase in As and Zn concentrations above background levels in this system was likely due to inputs from both mining and geological deposits.

## CHAPTER 4

### MERCURY TRANSFORMATION AND METHYL MERCURY PRODUCTION IN SOILS AND SEDIMENTS OF THE PRA RIVER BASIN

#### 4.1 Introduction

In aquatic systems, processes of mercury (Hg) methylation and methyl-Hg (MeHg) demethylation determine the state and the overall toxicity of Hg compounds. The occurrence of MeHg in soils, waters, and sediments within watersheds has led to a tremendous interest driven primarily by the ability of MeHg to bioaccumulate and to impact both ecological functions and human health (WHO, 1990; Lindqvist et al., 1991; Porcella, 1994; Rolfhus and Fitzgerald, 1995). As a neurotoxin, MeHg attacks the central nervous system (Lindqvist et al., 1991; Porcella, 1994). The principal pathway for human exposure to this toxic Hg compound is the consumption of Hg-contaminated fish, and this risk is of particular concern for fetuses and young children (Porcella, 1994). Accordingly, regulatory agencies focus on fish as the target organism to protect the health of humans and other sensitive organisms.

Mercury discharged to soils, waters, and sediments in gold mining-impacted watersheds such as the Pra River basin is primarily in the metallic form (Bonzongo et al. 1996). Once in these environmental compartments, the released  $\text{Hg}^0$  eventually undergoes transformations to produce readily bioavailable Hg-species (see Chapter 2). Methylation of  $\text{Hg}^{2+}$  produced by oxidation of the initially released  $\text{Hg}^0$  is an important step in environmental Hg cycling due to its ecological significance. Therefore, studies aimed at understanding the methylation of Hg under environmental conditions abound in

the literature. In such studies, researchers have experimentally measured the potential rates of Hg methylation and MeHg demethylation in water, soil, and sediment samples using different approaches. Hg methylation or MeHg demethylation studies have mainly been carried out by means of radiochemical procedures (e.g., Korthals and Winfrey, 1987 and Furutani and Rudd, 1980). A radioactive inorganic  $^{203}\text{Hg}$  isotope is added to the sediment, and after a pre-set anaerobic incubation time, MeHg is extracted and the amount of methylated  $^{203}\text{Hg}$  quantified. This technique has several limitations. The major drawback lies in the elevated Hg levels required to observe detectable reaction yields. All the same, due to the low specific activity of commercially available inorganic  $^{203}\text{Hg}$  used in these studies, the tracer must be added at concentrations at least 10 times higher than environmental Hg concentrations. This has an unknown effect on the microbial community and might favor the selection of mercury-tolerant strains of microorganisms. Because these experiments are based on the microbial response, the results observed are often not comparable to those obtained with the initial bacterial distribution. Furthermore, with the  $^{203}\text{Hg}$  approach, it is not possible to study demethylation and methylation reactions in the same sample. To overcome this limitation, labeled  $^{14}\text{CH}_3\text{Hg}$  instead of  $\text{CH}_3^{203}\text{Hg}$  was used to quantify the radioactive methane or carbon dioxide yield, which is known to be formed during demethylation of MeHg (Oremland et al., 1991). However, both methane and carbon dioxide can be incorporated into the microbial biomass, making the analytical protocol required extremely difficult and time consuming. Additional limitations of radiotracer techniques are associated with the necessary radioactive safety precautions and waste-handling procedures.

Studies have also used cold spikes (i.e. the addition of non radioactive Hg-compounds) of the most abundant isotope of Hg to assess the potential rates of Hg methylation and MeHg demethylation (e.g. Furtani and Rudd, 1980; Ramlal et al., 1986; Xun et al., 1987; Zhang and Planas, 1994; Chen et al., 1996; Bonzongo et al. 1996).

Drawbacks related to this approach are similar to the one described above, in that it adds very high Hg levels to the samples to obtain measurable reaction yields. In contrast, it is safer as it does not involve radioactivity and has the advantage of being cost-effective.

A recent improved procedure makes use of stable isotopes combined with inductively coupled plasma mass spectrometry (ICP-MS) technique. To measure and follow methylation rates, this combination offers several advantages. First, the response is not calculated from the total metal concentration but is based on the changes in the isotope ratio of the metal of interest. Isotope ratio measurements are very precise even at very low concentration levels due to the sensitivity of the analytical technique used, thus allowing very low spike concentrations that should preserve the bacterial community in the samples. Second, in all these experiments, the fate of the tracer added as well as the behavior of the naturally occurring metal already in the system can be monitored simply by following the different isotopes of that element. Third, demethylation rates can be measured together with methylation in the same sub-sample. To follow and unravel these coupled and often overlying processes, double-labeling tracers are necessary. Species-specific reactions are very sensitive, and the precision of speciated isotope dilution procedures can account for these difficult simultaneous mechanisms. This approach has been used recently by Hintelmann et al. (2000), Lambertsson et al. (2001) and Mauro et al. (2002). The high cost associated with this last technique, the use of tracer in Hg



transformation measurements share one problem common to all techniques that are currently available, the difficulty to mimic ambient Hg speciation with any kind of spike. Therefore, any of these techniques would allow determination of potential Hg transformation rates only, which are useful in predicting the tendency of a given systems to produce and accumulate methyl-Hg.

The Pra River basin is anthropogenically impacted with Hg that has been added to this aquatic system over several centuries, providing a well established gradient in Hg concentration and response. Hence, use of any of the above mentioned techniques would be adequate. For financial reasons, the less expensive technique based on non-radioactive Hg compounds was used in this study.

Data presented in Chapter 3 show levels of both total and methyl Hg concentrations in different environmental compartments of the Pra River basin. Regardless of the season, mercury (as total-Hg concentrations) is detected in all media, and variations in observed levels are primarily related to the proximity of the sampling sites to mining centers. With regard to methyl-Hg, and the fact that AGM in Ghana is more intense and wide spread in the dry season, its levels in soils, water, and sediment increase from the dry to the wet season. Consequently, it is apparent that hydrology plays a significant role in the observed concentration trends. Based on field data presented in chapter 3, it is hypothesized that methyl-Hg in the Pra River system is produced primarily in locations with Hg-contaminated soils and later introduced into waterways by storm water runoffs. The premise behind this hypothesis is that the saturation of Hg-contaminated soils with rain water leads to anoxic conditions that favor methyl-Hg formation, particularly in organic-matter containing soils. If verified, this would help explain the quasi

disappearance of methyl-Hg in nearly all compartments during the dry season in contrast to its occurrence at levels above the detection limit of the analytical procedure used in this study.

This research was designed to: (1) evaluate the effect of wet/dry cycles characteristics of the studied watershed on Hg already present in Pra River basin soils as well as on Hg added to these soils under controlled laboratory conditions; and (2) assess the ability of riverine sediments in the Pra River system to produce and accumulate methyl-Hg. The ultimate goal was to assess the ability of soils and sediments of the studied watershed to produce methyl-Hg as well as the potential for such produced methyl-Hg to bioaccumulate and biomagnify in food chains.

## **4.2 Materials and methods**

### **4.2.1 Study Area and Sampling**

A description of the study area, the Pra River basin, is given in Chapter 3. The sampling locations are in southwestern Ghana (Figure 3-2).

Surface sediment and soil samples (top 0 to ~10cm) collected during the dry season were used in this study. The study was intentionally limited to randomly selected sites representative of the studied river basin. From the sampling locations shown on Figure 3-2 (Chapter 3), only samples collected from the following sites were used: (i) River Offin (site # 10, 12, and 14); (ii) the Upper Pra (sites 17 and 19); and (iii) the Lower Pra (site # 2, 3, 4, 6, and 8). Sediment and soil samples were collected following metal free ultra clean techniques. The samples were collected using acid-cleaned Teflon coated scoops and placed in acid washed polyethylene containers and/or re-sealable bags. Samples earmarked for Hg transformations studies were not frozen but maintained on ice in a cooler during sample collection and transport. Samples were shipped by express courier

to the laboratory at the University of Florida, Gainesville where all analyses were conducted.

#### **4.2.2 Determination of the Effect of Water Content on Methyl-Hg Formation in Soil**

In heavily vegetated tropical watersheds, the presence of organic matter in soils, in combination with increasing moisture content, can drive the production of methyl-Hg in the rainy season by favoring development of anoxic conditions and proliferation of Hg-methylating microbes. To verify this assumption, soil samples collected from the selected sites during the dry season were sieved (1mm mesh) to yield homogenous fine soils. About 1g of fine materials was weighed in capped tubes, spiked with nano-pure water to create different soil:water ratios and to establish a gradient of water content. The headspace was then flushed with N<sub>2</sub> to expedite the development of anoxic conditions. Next, the tubes were capped and incubated at room temperature. In a second set of experiments, a similar approach was used, except that in addition to water, soil samples were also spiked with Hg (as HgCl<sub>2</sub>) to bring the final concentration of total-Hg in the sample mixture to a value corresponding to the sum of total-Hg already present plus an additional 1 µg/g of dry sediment. In all cases, duplicate samples were prepared along with controls (i.e. not spiked with water for the first set and no Hg added for the second set). The samples were allowed to incubate for 30 days and at the end of the incubation period, they were frozen at -18°C until analysis. Methyl-Hg was extracted by alcohol/alkaline digestion and analyzed using a procedure adapted from Bloom (1989). Details on this analytical technique are given in Chapter 3. Calculated potential rates as ng Hg g<sup>-1</sup> day<sup>-1</sup> were obtained by dividing the averaged measured methyl-Hg concentrations over the incubation period of 30 days for the different soil-water

saturation. Data obtained from these experiments are presented in Figures 4.2 through 4.9 and discussed in the results section.

#### **4.2.3 Determination of the Potential Rates of Hg Methylation and Methyl-Hg Degradation in Riverine Sediments**

The potential rates of Hg methylation and methyl-Hg degradation were determined according to the method of Pak and Bartha (1998). Sediment samples from the 8 selected sites were sieved (1mm mesh) to yield homogenous fine materials, then used to prepare slurries by dilution with deionized water (1:1; mass per volume). The obtained slurries were amended with  $\text{HgCl}_2$  to a final concentration of  $1\mu\text{g Hg mL}^{-1}$  for methylation (M) experiments, or  $0.01\mu\text{g Hg mL}^{-1}$  for demethylation (D) experiments (with methyl-Hg added as  $\text{CH}_3\text{HgCl}$ ). In all cases, samples were deoxygenated with ultra high purity (UHP)  $\text{N}_2$  for 20 min, capped and incubated in the dark for 5 to 8 days. Control slurries were not spiked with Hg compounds to allow the determination of the change in Hg speciation based on the background levels of Hg previously present in the sample. At periodic intervals, 2 vials were sacrificed for MeHg analysis by storing at  $-18^\circ\text{C}$  prior to extraction and analysis. Methyl-Hg was then extracted from slurries and analyzed by CV-AFS following Bloom's procedure (1989) described earlier in Chapter 3. The QA/QC criteria on these analyses are also given in Chapter 3 and Appendix A.

#### **4.2.4 Determination of Hg Speciation in Soil and Sediment Samples**

To determine the distribution of Hg amongst different soil/sediment mineral and organic fractions, an operationally defined extraction procedure adapted from Bloom et al. (2003) was used. The concept is that, exposure to increasingly powerful solvents will dissolve and extract Hg-containing species from a sample in a stepwise manner congruous with the relative solubilities of the Hg-containing phases present. The

approach also helps to assess the availability of Hg to methylating agents in soils/sediments by correlating the different Hg fractions to either potential methylation rates or ambient methyl-Hg levels. The Hg speciation technique used is based on selective extractions using ultra-clean techniques to minimize contamination. Two (2) grams of sieved soil/sediment were extracted sequentially (Figure 4-1) with 5 different solutions following the flow chart presented in Fig. 4.1 and discussed below.

- *Fraction 1 (F1):* This fraction is operationally defined as the acid soluble fraction, represented mainly by the solubilization of complexes such as HgO and HgSO<sub>4</sub>. This fraction is extracted with a mixture of 0.1 M glacial acetic and concentrated 0.01 M HCl.
- *Fraction 2 (F2):* Organo-complexed fraction, predominantly Hg bound humics, was extracted by solubilization in a 1 M KOH solution.
- *Fraction 3 (F3):* Strongly complexed fractions such as Hg bound to amorphous organo-sulfur, Hg-amalgams, or crystalline Fe/Mn oxide phases were extracted using 12 M solution of HNO<sub>3</sub>
- *Fraction 4 (F4):* This fraction removes Hg associated with sulfide minerals. The solubilization is done with aqua regia (mixture of concentrated HNO<sub>3</sub> and HCl in 1:3 ratio)
- *Fraction 5 (F5):* After removal of all the above fraction, the remaining Hg in the solid matrix is believed to be part of the structure of minerals such as aluminosilicates. To dissolve such Hg fractions, a hot (110°C) digestion using a mixture of HF, HNO<sub>3</sub> and HCl is required.

The extraction process was conducted by mixing 6 ml of extractant solution with 2g of solid sample in a glass vial and rotary shaken for 18-20 hours, with end-over-end tumbling. The vials were then centrifuged at 2000 rpm for 15 min, and the supernatant liquid decanted and filtered (0.45µm). Each step of the extraction procedure except the

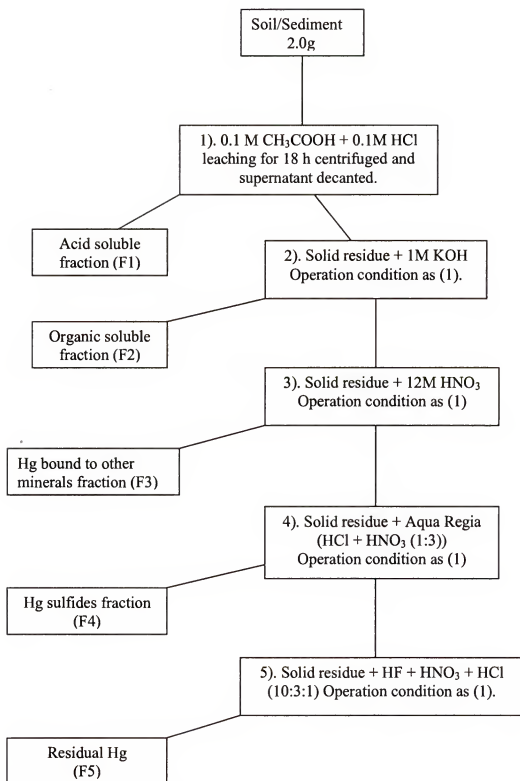


Figure 4-1: Schematic flow chart of the sequential extraction of Hg in soil/sediment.

final step (F5) (see Figure 4-1) was rinsed with the extractant solution before solubilizing the next fraction. In each case, the supernatant was used to determine the concentration of total-Hg solubilized. To do so, fractions F1, F2, and F3 were digested overnight with 0.2M BrCl (bromine monochloride) at room

### **4.3 Results and Discussion**

#### **4.3.1 Effect of Water Content on Inorganic Hg Present in Soils and on Hg Newly Added to Soils**

In southwestern Ghana, AGM is very intense and wide spread in the dry season. The latter corresponds to the period of high Hg introduction to different environmental compartments. Despite the presence of detectable total-Hg concentrations in soil samples collected during the dry season, methyl-Hg levels were mostly below the analytical detection limit (Table 3-10 in Chapter 3). To some extent, a similar observation was true for data obtained on sediment and water samples collected during the same period. On the other hand, the co-occurrence of methyl-Hg above detectable levels in soils, water, and sediment samples collected during the wet season suggested that MeHg in these environmental compartments could have a major common source, likely associated with the effect of rain. This hypothesis was confirmed by data presented in Figures. 4-2 through 4-9.

Examination of these graphs led to the following observations. First, in both non-spiked and Hg-spiked water treated soils, there was a general increasing trend in potential rates of methyl-Hg production with increasing water content. Therefore, the addition of water to soil loaded with inorganic Hg stimulated the transformation of Hg and the production/accumulation of methyl-Hg. As the water content reached saturation (100%),

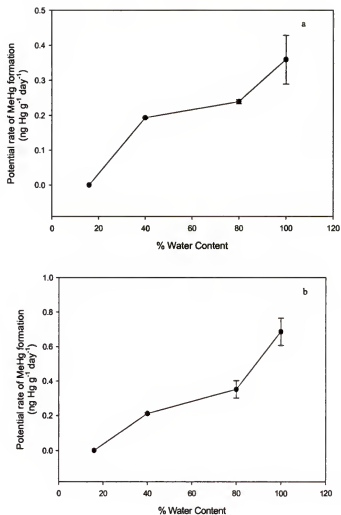


Figure 4-2. Potential rates of Hg methylation in soils collected from Lower Pra (site 2).

- (a): soils spiked with different levels of water to create a water content gradient
- (b): soils spiked with both water (similar to (a)) and Hg<sup>2+</sup>.



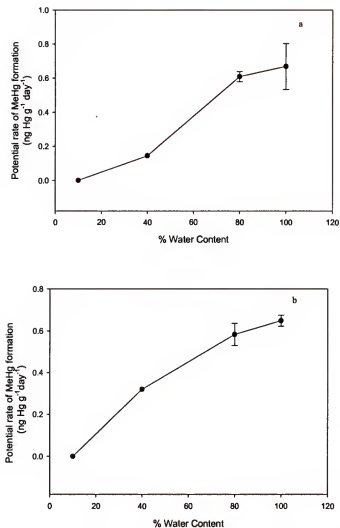


Figure 4-3. Potential rates of Hg methylation in soils collected from Lower Pra (site 4).

- (a): soils spiked with different levels of water to create a water content gradient
- (b): soils spiked with both water (similar to (a)) and Hg<sup>2+</sup>.

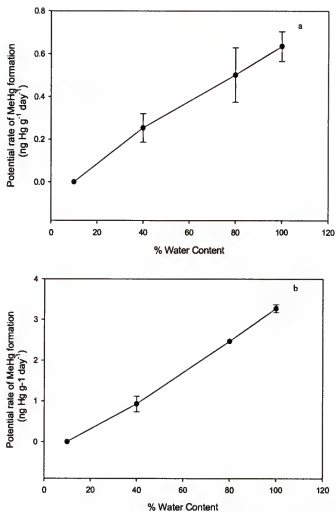


Figure 4-4. Potential rates of Hg methylation in soils collected from Lower Pra (site 6).

- (a): soils spiked with different levels of water to create a water content gradient
- (b): soils spiked with both water (similar to (a)) and Hg<sup>2+</sup>.

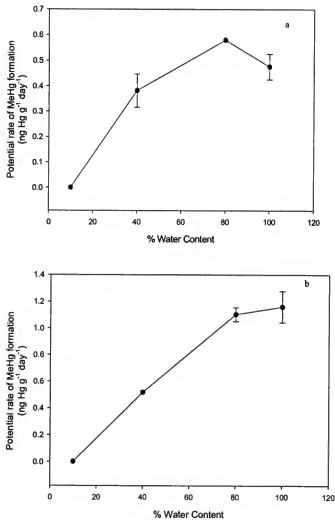


Figure 4-5. Potential rates of Hg methylation in soils collected from Lower Pra (site 8).

- (a): soils spiked with different levels of water to create a water content gradient
- (b): soils spiked with both water (similar to (a)) and Hg<sup>2+</sup>.

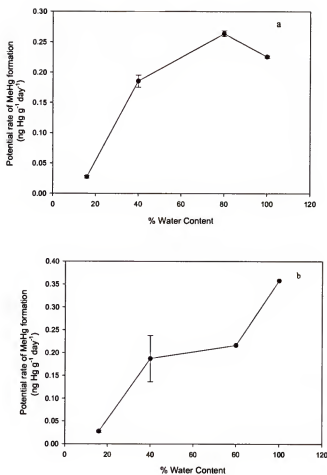


Figure 4-6. Potential rates of Hg methylation in soils collected from Upper Pra (site 17).

- (a): soils spiked with different levels of water to create a water content gradient
- (b): soils spiked with both water (similar to (a)) and Hg<sup>2+</sup>.

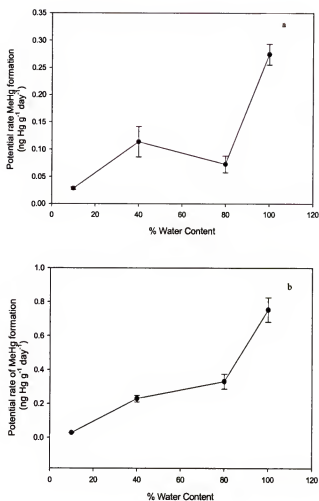


Figure 4-7. Potential rates of Hg methylation in soils collected from Upper Pra (site 19).

- (a): soils spiked with different levels of water to create a water content gradient
- (b): soils spiked with both water (similar to (a)) and Hg<sup>2+</sup>.

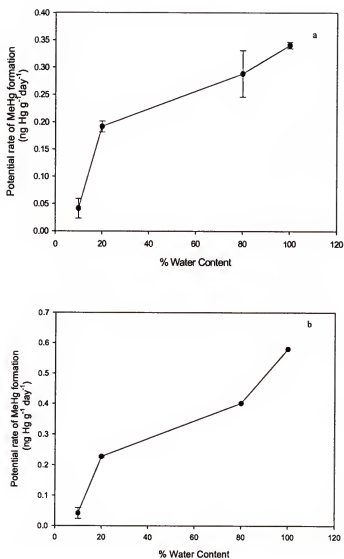


Figure 4-8. Potential rates of Hg methylation in soils collected from River Offin (site 10).

- (a): soils spiked with different levels of water to create a water content gradient
- (b): soils spiked with both water (similar to (a)) and  $\text{Hg}^{2+}$ .

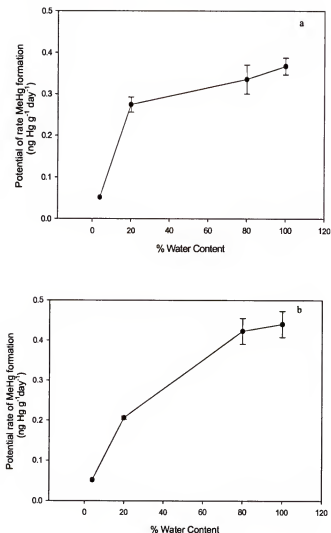


Figure 4-9. Potential rates of Hg methylation in soils collected from River Offin (site 12).

- (a): soils spiked with different levels of water to create a water content gradient
- (b): soils spiked with both water (similar to (a)) and Hg<sup>2+</sup>.

slurries were obtained and the rates of methyl-Hg production reached their maximum. As suggested earlier, this was likely due to the water-driven development of anaerobic conditions associated with the oxidation of organic matter present in soils. Indeed, in both sediments and soils, production of methyl-Hg was coupled with anoxic decomposition of

organic matter, with sulfate reduction as the predominant microbial-driven process linked to methyl-Hg production in most soils and sediments (Compeau and Bartha, 1985; Gilmour et al., 1992; Devereux et al. 1996; King et al., 2002).

Figure 4-10 gives a simplified but comprehensive representation of the redox ladder in sedimentary environments and identifies regions where different terminal electron acceptors get involved in the degradation of organic versus the  $E_h$  of the system.

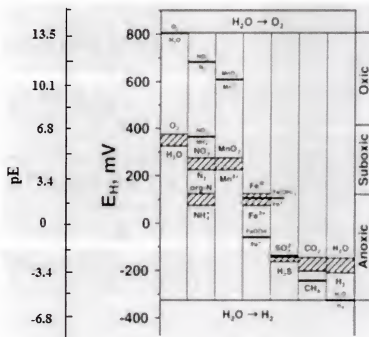


Figure 4-10. Observed transformation of oxidized to reduced species along the redox ladder in soils (adapted from Sposito, 1989). The  $E_h$  values, the redox transformations theoretically predicted to occur are indicated by horizontal lines. The oxidic ( $E_h > 414$  mV), suboxic ( $120 < E_h < 414$  mV) and anoxic ( $E_h < 120$  mV) boundaries are indicated.

Previous studies investigating the production of methyl-Hg in soils and sediments point to suboxic and mostly anoxic conditions as prerequisites for methyl-Hg formation in natural systems (Sposito, 1989).

In reducing environments, dissolution of certain oxide minerals, primarily Mn and Fe oxyhydroxides releases Hg and other metals adsorbed onto them, thereby increasing



Hg bioavailability to methylating microorganisms. However, reduction of sulfate and precipitation of Hg sulfides can limit such bioavailability, except under conditions that favor the presence of neutrally charged aqueous mercury sulfide species (Benoit et al. 1999 and 2001). Second, with few exceptions (i.e. data obtained from Lower Pra sites # 6 and #8), no significant differences were observed in the recorded potential methylation rates for the different water content levels, regardless of the initial Hg content of the soils (e.g. non-spiked versus Hg-spike soils). This suggested that the newly added Hg under laboratory conditions did not add significantly to the bioavailable Hg fraction of the Hg already present in the soil. Therefore, production of methyl-Hg in soil/sediment is controlled primarily by availability of the different Hg fractions. The operationally defined sequential extraction described earlier was used to link measured potential Hg-methylation rates to the different mineral and organic Hg fractions present in tested soils. The results of this speciation are presented in Table 4-1. Use of simple linear regressions to correlate the different Hg fractions to the measured rates of methyl-Hg production showed that the Hg fractions solubilized by KOH and aqua regia (see flow chart of Figure 4-1) make most of the bioavailable Hg fraction (e.g., Figure 4-11a and b). All other operationally defined fractions gave rather scattered plots with no statistically significant relationships between Hg content and rates of methyl-Hg production. If production of methyl-Hg is taken as a surrogate of Hg availability, the significant relationships between potential rates of methyl-Hg production and KOH and aqua regia fractions can be explained as follows: KOH solubilizes Hg that is bound to organic matter. Therefore in soils, as the organic matter undergoes degradation, it releases previously trapped Hg, making it available to methylating agents. Unlike the KOH

fraction, the correlation obtained between the potential rates of Hg methylation and the sulfide fraction (aqua regia) is more complex. Interestingly, production of methyl-Hg in anoxic soils and sediments has been linked primarily to sulfate reducing bacteria. When considered in combination with the pE or Eh/pH diagram of Hg, the presence of sulfur could result in the formation of neutrally charged aqueous complexes of Hg and S (e.g.  $\text{Hg}(\text{HS}_{2\text{aq}}^0)$ ), which are easily methylated by sulfate reducing bacteria, due to the ability of neutrally charged aqueous Hg-compounds to cross cell membranes (Benoit et al, 2001a; Benoit et al., 1999).

Table 4-1. Total mercury concentrations (ng Hg g<sup>-1</sup> dry weight) and percentage of species contribution in the investigated soils, along Pra River Basin

Site #	F1 CH <sub>3</sub> COOH + HCl (ng/g)	F1 %	F2 KOH (ng/g)	F2 %	F3 HNO <sub>3</sub> (ng/g)	F3 %	F4 Aqua Regia (ng/g)	F4 %	F5 HF + HCl + HNO <sub>3</sub> (ng/g)	F5 %	Amount Extracted (ng/g)	Amount Before Extraction (ng/g)	% THg Extracted
Lower Pra													
2	1.43	18.72	4.61	60.34	0.72	9.42	0.33	4.32	0.55	7.20	7.64	10	76.4
4	1.26	11.56	4.86	44.59	1.96	17.98	1.86	17.06	0.96	8.81	10.9	15	72.67
6	279.7	34.16	409.4	50.00	58.7	7.17	50.19	6.13	20.84	2.55	818.83	1106	74.04
8	2.41	22.97	5.83	55.58	1.06	10.10	0.78	7.44	0.41	3.91	10.49	15	69.93
River Offin													
10	4.75	21.12	10.14	45.09	4.71	20.94	1.14	5.07	1.75	7.78	22.49	28	80.32
12	2.9	24.64	6.78	57.60	0.75	6.37	0.8	6.80	0.54	4.59	11.77	16	73.56
Upper Pra													
17	6.24	25.37	15.58	63.33	1.36	5.53	0.81	3.29	0.61	2.48	24.6	31	79.35
19	1.3	19.23	4.07	60.21	0.63	9.32	0.59	8.73	0.17	2.51	6.76	9	75.11

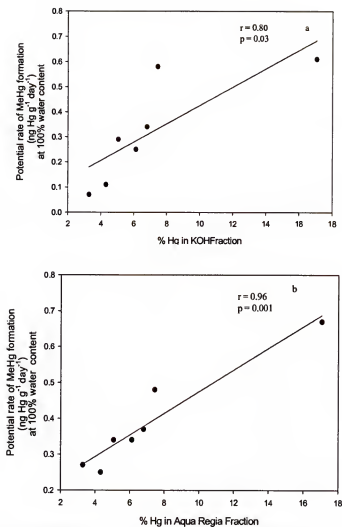


Figure 4-11. Effect of mercury speciation on MeHg formation - Correlation of MeHg formed with: a = % Hg in KOH fraction and b = % Hg in Aqua regia fraction at 100 % water saturation.

#### 4.3.2 Production and Degradation of Methyl-Hg and the Potential for Mercury Accumulation in River Sediments

The ability of sediment samples collected from the above selected sites to accumulate methyl-Hg was assessed through a series of laboratory incubations. Rates of methyl-Hg production and demethylation in sediment were calculated as  $\text{ng CH}_3\text{Hg}^+$  produced/demethylated per gram sediment per hour. The following calculation (Eq. 4.1.) was used in this study, and obtained data are presented in Table 4-2:

$$\text{Methylation Rate} = \frac{\text{ng Hg methylated}}{\text{gram}_{\text{sediment}} \times \text{incubation hours}} \quad \text{Eq. 4.1}$$

The methyl-Hg demethylation rates were calculated similarly to the above shown Hg-methylation example.

Table 4-2. Potential rates of mercury methylation and methyl-Hg demethylation in sediments of the Pra River Basin

Sampling sites #	Potential rates of Hg- methylation (M) ( $\text{ng.g}^{-1}.\text{hr}^{-1}$ ) (average ( $n=3$ ) $\pm$ 1SD)	Potential rates of MeHg- demethylation (D) ( $\text{ng.g}^{-1}.\text{hr}^{-1}$ ) (average ( $n=3$ ) $\pm$ 1SD)
Lower Pra #6	$0.1132 \pm 0.0267$	$0.1312 \pm 0.0172$
Offin #12	$0.0522 \pm 0.0049$	$0.0666 \pm 0.0032$
Offin #14	$0.3643 \pm 0.1138$	$0.1679 \pm 0.0197$
Lower Pra #2	$0.1443 \pm 0.0171$	$0.0700 \pm 0.0158$
Lower Pra #8	$0.3380 \pm 0.0288$	$0.1646 \pm 0.0322$
Lower Pra #3	$0.1863 \pm 0.0345$	$0.0040 \pm 0.0006$
Upper Pra #19	$0.2678 \pm 0.0226$	$0.2085 \pm 0.0305$

In general, these rates were of the same order of magnitude, except for rates obtained from samples collected from sites 12 (on River Offin), 2, and 3 (on the Lower Pra). In addition, they compare very well with the numbers reported in the literature based on the use of tracer techniques (e.g., Rodríguez Martín-Doimeadios et al., 2004)

Since calculation of potential Hg transformation rates as presented above does not take into account the amount of Hg added to the sample, a normalization by calculating the specific rates of Hg methylation and methyl-Hg demethylation, i.e., the percentage of the added inorganic Hg (for methylation experiments) and methyl-Hg (for demethylation) per gram sediment per incubation hour as shown in Eq. 4.2. is usually used.

$$\text{Specific Methylation Rate (K}_M\text{)} = \frac{100 \times \text{Hg Methylation Rate}}{\text{ng Hg added} \times \text{g}} \quad \text{Eq. 4.2.}$$

Table 4-3. Specific rates of Hg methylation and methyl-Hg demethylation determined as percentage of the added inorganic Hg (for methylation experiments) and methyl-Hg (for demethylation) transformed per incubation hour

Sampling sites #	Specific Hg methylation rates (%.hr <sup>-1</sup> )	Specific methyl-Hg demethylation rates (%.hr <sup>-1</sup> )
Lower Pra # 6	0.0113	1.3093
Offin #12	0.0052	0.6646
Offin #14	0.0364	1.6756
Lower Pra # 2	0.0144	0.6986
Lower Pra # 8	0.0338	1.6427
Lower Pra # 3	0.0186	0.0399
Upper Pra #19	0.0268	2.0808

The specific rate of methyl-Hg demethylation was calculated similarly to the above shown calculation for specific Hg-methylation rate, and the corresponding data appear in Table 4-3. Based on these calculations, the ability of tested sediments to produce methyl-Hg is

quite similar across the watershed. However, these sites (6, 8, 14, and 19) show higher potential for methyl-Hg degradation ( $>1\% \cdot \text{hr}^{-1}$ ) than the other 3 sites in this study.

The tendency towards equilibrium between methyl-Hg production and its degradation in such systems can be assessed by determining the “net potential” of Hg transformation. The methylation (M) to demethylation (D) ratios is often used as a parameter to characterize such a tendency. Accordingly, M/D ratios were calculated by dividing methylation to demethylation rates. This is a measure of the relative importance of methylating and demethylating activities and is useful in identifying potential conditions of accelerated methyl-Hg production (Ramlal et al., 1986). The M/D results are presented in Figure 4-12. These data show clearly that within the watershed studied, there are sites with high potential to produce and thereby accumulate methyl-Hg (i.e.  $M/D > 1$ ). While no equal rates were found for both M and D (i.e.  $M/D = 1$ ), a few sites exhibited M/D ratios below 1, suggesting a high potential for degradation of any produced methyl-Hg and lower chances for methyl-Hg accumulation. Unfortunately, based on the data presented here, an estimate of the net product of Hg methylation and MeHg demethylation at the watershed scale is not possible. It is likely that in this highly hydrodynamic aquatic system, the bioaccumulation of produced methyl-Hg in organism inhabiting the river section is limited by methyl-Hg export towards the river delta and the Gulf of Guinea as a consequence of torrential tropical rains characteristics of the region under study.

It is interesting to note that in addition to the above used approaches, rate constants (K) are also often used to compare M and D processes. Specific methylation and demethylation rate constants ( $K_m$  and  $K_d$ ) can be calculated: (1) by taking into account

the data obtained in the experiments and assuming pseudo-first order reaction kinetics, or (2) by using the whole data set and considering a reversible reaction kinetic model. The pseudo-first order reaction kinetics allows the calculation of the methylation constant for Hg ( $K_m$ ) and the demethylation constant ( $K_d$ ) for methyl-Hg. Such a model can be used to describe Hg transformation reactions.

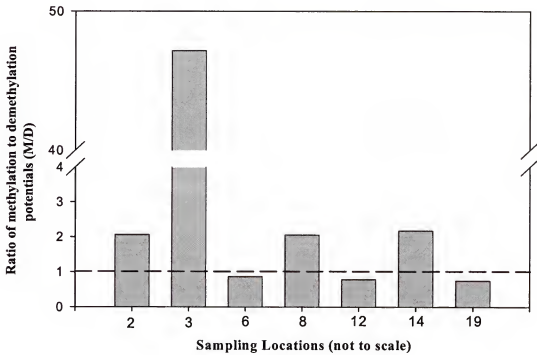


Figure 4-12. Ratios of potential rates of Hg methylation (M) to methyl-Hg demethylation (D) for sediment samples shown in Table 4-2.

Because of the co-occurrence of M and D, the net production of methyl-Hg can be written as follows:

$$\frac{d[CH_3Hg^+]}{dt} = K_m [Hg^{2+}] - K_d [CH_3Hg^+] \quad (4.3)$$

where  $[CH_3Hg^+]$  = concentration of methyl-Hg newly generated from the added  $Hg^{2+}$ ,  $K_m$  is the specific methylation rate constant in  $hours^{-1}$ ;  $[Hg^{2+}]$  = concentration of added



inorganic Hg,  $K_d$  = specific demethylation rate constant in hours<sup>-1</sup> and  $t$  = incubation time in hours. Equation (4.3), written here for added inorganic Hg, holds also for added methyl-Hg.

Therefore, from the experimental data,  $[\text{CH}_3\text{Hg}^+]$  is low enough so that the second term in Eq. (4.3) is much smaller than the first one. After elimination of that second term and integration, Eq. (4.3) reduces to:

$$K_m = \frac{[\text{CH}_3\text{Hg}^+]}{[\text{Hg}^{2+}] \times t} \quad (4.4)$$

When  $\text{CH}_3\text{Hg}^+$  is spiked to the sediment, the  $\text{Hg}^{2+}$  resulting from the demethylation of added methyl-Hg is virtually zero at the beginning of the experiment. In this case, equation would then reduce to:

$$\frac{d[\text{CH}_3\text{Hg}^+]}{dt} = -K_d [\text{CH}_3\text{Hg}^+] \quad (4.5)$$

which is readily integrated to:

$$[\text{CH}_3\text{Hg}^+] = [\text{CH}_3\text{Hg}^+]_0 e^{-k_d t} \quad (4.5)$$

where  $[\text{CH}_3\text{Hg}^+]_0$  is the initial concentration of  $\text{CH}_3\text{Hg}^+$  in the sediment. The specific demethylation rate constant  $K_d$  is then obtained by linear regression of  $\text{Ln}[\text{CH}_3\text{Hg}^+]$  versus time ( $t$ ). If the reaction follows a first order kinetics, then the half-life time ( $t_{1/2}$ ) of methyl-Hg in sediment can be calculated using equation 4.6.

$$t_{1/2} = \frac{\text{Ln}2}{K_d} \quad (4.6)$$

In applying the kinetics approach described above with the experimental data obtained in this study, the following is observed. The determination of  $K_m$  based on equation 4.4

gives  $K_m$  values ranging from  $5.0 \times 10^{-5}$  to  $1.01 \times 10^{-3} \text{ h}^{-1}$ . These fall within the reported in the literature for estuarine sediments (Rodríguez Martín-Doimeadios et al., 2004). In contrast, plotting  $\text{Ln}[\text{CH}_3\text{Hg}]$  versus time to determine  $K_d$ , the slope of the linear regression resulted in trends not characteristics of first order reactions. Indeed, in methyl-Hg degradation experiments, decomposition of added methyl-Hg was very quickly (first 60 hours) surpassed by production of methyl-Hg from probably the methylation of both the inorganic Hg already present in the sediments and the fraction released from the degradation of added methyl-Hg. The use of this approach would have been appropriate if detailed measurements were made in the first 24 hours. Over the length of one week, the obtained data simply favor methylation over demethylation.

In conclusion, these laboratory investigations confirmed the importance of soil hydration in methyl-Hg production in the studied watershed. Therefore, in the Pra River basin, methylation of Hg takes place primarily during the rainy season in Hg-contaminated soils. This production accounts for most of methyl-Hg recorded in the aqueous phase.

Finally, the difference in rates of methyl-Hg production versus its degradation suggests that methyl-Hg can be produced and accumulated in this aquatic system. The river delta and the Pra River estuary would likely make good sites for studies on Hg bioaccumulation as most of the Hg transported by fluvial processes would eventually reach and accumulate in these depositional areas.

## CHAPTER 5 ASSESSING THE ROLE OF SOLAR RADIATION ON MERCURY TRANSFORMATION AND CYCLING

### 5.1 Introduction

The amount of UV radiation reaching the surface of the earth is highly variable as it is influenced by many factors. These are geometric factors (time of day, latitude, altitude, season, and earth-sun distance), atmospheric factors (ozone concentration, clouds, and other gases in the atmosphere such as NO<sub>2</sub> and other pollutants) and the earth's albedo (which causes solar radiation to bounce between the surface and the atmosphere). Hence, the large variations in UV radiation reaching the earth's surface are due to the geometry of earth-sun system. Season and latitude play a very key role in attenuation of solar radiation by controlling solar zenith angles (SZA) and thereby the thickness of the air column through which radiation must pass before reaching the ground (Allen et al., 1998; Diaz et al., 2000; Whitehead et al., 2000). For instance, a change in solar zenith angle from 55° to 75° implies doubling of air mass. Therefore solar radiation including UV is highest and least in the tropics and decreases at higher altitudes (Weiler and Penhale, 1994; Allen et al., 1998; Diaz et al., 2000; Whitehead et al., 2000). The next factor responsible for large changes in the total flux of UV (290-400 nm) is ozone concentration. About 90% of total ozone is located in the stratosphere where it is constantly created and destroyed. However, total column ozone also displays large geographic and temporal variations, hence varying with latitude. Though most ozone is formed near the equator, the total column ozone is lower (250-300 DU) in tropical

regions than at higher latitudes. The result is the higher solar irradiances in the tropics than the temperate regions (Madronich, 1995; Allen et al., 1998; Diaz et al., 2000).

The solar energy of most interest to environmental chemistry is the UV component of sunlight. Below 290nm, solar radiation is significantly absorbed by a thin stratospheric ozone layer that surrounds the Earth at an altitude of about 30-40 Km above the Earth's surface, while above 400nm it does not provide enough energy to break most chemical bonds. In the past, production and use of chlorofluorocarbons (CFCs) for refrigerants, aerosol propellants, and foamed plastics resulted in a sharp increase of CFCs in the atmosphere. Chlorofluorocarbons are very resistant to tropospheric breakdown and they readily diffuse into the stratosphere where they dissociate photochemically to provide chlorine atoms (Crosby, 1998). The result is a cyclic process in which, a small amount of chlorine atoms could destroy a lot of ozone molecules. Initially, the thinning of the ozone layer was observed only at the poles where chlorinated chemicals concentrated, but later measurements revealed as much as 10% ozone loss at lower latitudes (Frederick, 1993; Crosby, 1998). From these observations, industrialized nations reacted by reducing use of the worst CFC offenders and planned to end the use of these chemicals altogether. Currently, CFCs are being substituted by oxidizable hydrofluorocarbons, such as 1,1,1,2-tetrafluoroethane (HFC-134a), and the atmospheric concentrations of several of the most prevalent organochlorine compounds such as  $\text{CHCl}_3$  and  $\text{CCl}_4$  have started to decline. Unfortunately, concentrations of the newer HFC are increasing sharply, an indication that the battle for a stabilized ozone layer is far from over (Crosby, 1998).

Solar radiation, directly or indirectly provides the primary driving force for biogeochemical cycles. Most of the solar radiation that reaches the earth is converted into

thermal energy, but the fraction in the UV and visible region, is diverted into photochemical and photo-biological processes that affect biogeochemical cycles.

*Therefore these processes are sensitive to changes in ground level solar radiation, which could result from global changes in stratospheric ozone.* Declines in stratospheric ozone and subsequent increases in solar UV-B radiation reaching the Earth's surface have been particularly pronounced during the past few decades. These changes, coupled with a number of recent findings that document the Earth's global warming could affect rates of natural organic matter (NOM) decomposition, the cycling of C and that of NOM-bound contaminants. Photo-degradation of NOM, such as humic substances, to produce molecules of lower molecular weight has been documented (e.g. Wetzel et al. 1995; Engelhaupt et al., 2002; Brinkmann et al., 2003). In most aquatic systems, between 50 and 90% of dissolved organic carbon (DOC) consist of humic substances, which are macromolecules with complex and heterogeneous structures (Artinger et al., 1999). In addition, depending on the geochemical surroundings, all natural waters could contain organic compounds with DOC concentrations ranging from about 0.1 to more than 100mg dissolved carbon per liter (Artinger et al., 1999). These organic compounds originate from both in situ (autochthonous) and external (allochthonous) sources; the latter being mostly from decomposing terrestrial plants.

Following the recognition of ozone depletion and increased solar UV radiation reaching the earth's surface, several investigations have been conducted, focusing mainly on potential effects of UV on (1) the productivity of terrestrial and aquatic plants; (2) the biogeochemical cycling of nutrients; and (3) several human health issues such as increased skin cancer, suppression of the immune system, and ocular damage (Van der

Leun et al., 1995). However, very little research has been directed toward the impact of UV radiation on trace metals and other contaminants bound to NOM. One such metal with serious environmental implications is mercury (Hg). Mercury is a particle-reactive element, which has a very strong affinity for organic ligands (Andrea, 1986), and formed Hg-organic matter complexes are very stable, with binding constants (K) in the order of  $10^{11.4}$  to  $10^{13.2}$  in the case of dissolved organic matter isolated from the Florida Everglades (Benoit et al. 2001). Interest in the environmental fate of Hg originates from the toxicity of its alkyl-compounds, namely methyl-Hg, which accumulates in biota, biomagnifies in food chains, and attacks the nervous system, with serious consequences on human health.

Field and laboratory studies of the effects of UV-B on metals have been very limited. In aquatic systems, it has been reported that UV-radiation enhances the reductive dissolution of Fe and Mn oxides/hydroxides in oxygenated waters, resulting in the conversion of the thermodynamically stable, but biologically unavailable, oxides of Fe and Mn into more bio-available species (Sunda and Huntsman, 1990; Waite and Szymczak, 1994). The reduction/solubilization of manganese and iron from their oxides/hydroxides can also be linked to the activity of Mn-and-Fe-reducing bacteria. From these observations, one can speculate that reported strong associations between Hg and Fe in oxygenated surface freshwaters (Bonzongo et al. 1999; Mastrine et al., 1999), suggest the existence of a pool of non available Hg that can become available to both biotic and abiotic processes following the photo and microbial induced dissolution of Hg adsorbed on oxides of Fe and Mn. This could be a beneficial process when released metals are those required as nutrients. In contrast, high levels of most metals would

probably result in increased toxicity to aquatic organisms. Finally, increased UV-B radiation could directly depress microbial activity in surface layers of water bodies, and data obtained by studying the cycling of Mn show that UV-related inhibition of the microbial oxidation of soluble Mn (II) to low-solubility Mn(IV) oxides favors the accumulation of Mn(II) in top layers of the epilimnion (Sunda and Huntsman, 1990).

The objective of this research were (i) to review the literature on the impact of increasing solar UV-B radiation reaching the earth's surface via NOM decomposition and subsequent effects on the biogeochemistry and cycling of Hg; (ii) to use the findings from (i) to carry out a preliminary laboratory study to assess the indirect effect of UV-B on Hg transformation. Obtained data will help predict the fate of aqueous Hg in organic rich tropical systems such as the Ghanaian Pra River system.

## **5.2 Changes in In-coming Solar Radiation and Mercury Cycling**

Photochemical changes can be divided into three stages: (1) the absorptive act during which the absorption of radiation of certain wavelengths occurs resulting in the production of an excited state, (2) primary photochemical processes involving the transformation of the electronically excited state and its de-excitation; and (3) secondary or "*dark*" reactions of the various species that have been produced by the primary photochemical processes.

With regard to the aquatic cycling of Hg, past and current research efforts have focused on reduction of  $\text{Hg}^{2+}$  and oxidation or volatilization of  $\text{Hg}^0$  in photic zones, i.e. stages 1 and 2 (e.g. Kim and Fitzgerald, 1986; Mason et al. 1994; Amyot et al. 1994; Xiao et al. 1991; Costa and Liss, 1999 and 2000; Lalonde et al. 2001; Beucher et al., 2002). Overall, little effort has been put on the above-described stage 3. Accordingly emphasis

is on gaps in our current knowledge of potential impacts of increasing UV-B radiation and temperatures on natural organic matter and the fate of Hg associated to NOM.

Based on the well-documented strong association between organic matter and Hg in natural systems, one could hypothesize that observed increasing trends in solar UV radiation reaching the earth's surface would affect the availability of Hg to both biotic and non-biological processes. Such impacts would be driven by the effect of UV on decomposing organic matter, hence, impacting the biogeochemical cycling of both C and Hg, as well as Hg toxicity. This impact would vary with factors such as the type of organic matter undergoing decomposition (allochthonous versus autochthonous), the chemical nature of organic matter, radiation intensity, and certain site-specific conditions such as pH, salinity, turbidity, etc. The premise behind this overall hypothesis is described in more detail below.

### **5.2.1 Organic Matter and Hg Association in Terrestrial and Aquatic Systems**

Historical increase in Hg emissions and subsequent atmospheric Hg deposition over terrestrial and aquatic landscapes has resulted in increased Hg burden of soils and sediments in both urban/suburban and pristine environments. In North America, Hg pollution has been linked to both temporal patterns of its consumption in gold and silver mining in late 1800's and early to mid 1900's, and industrial activities in modern times (Nriagu, 1994). The fate of Hg introduced into aquatic systems seems to be sedimentation and burial as ascertained by the study of historic fluxes (e.g., Swain et al., 1992; Landers et al., 1998; Pirrone et al., 1998). However, the fate of the Hg fraction, which accumulates on terrestrial catchments, remains poorly understood. Terrestrial soils store more organic matter in the upper meter than is present in either the atmosphere or living carbon pools (Schlesinger, 1991). After its deposition on landscapes, Hg is quickly



bound, but not irreversibly, to the organic matter and soil particles (Johansson and Iverfeldt, 1994; Lee et al., 1994; Lodenius, 1994). Vegetated soils are usually characterized by the presence of a top organic-rich layer produced by decomposing litter, and this organic matter has a very high affinity for most trace metals, including Hg, which bonds strongly to NOM to produce true organo-Hg compounds (Andrea, 1986; Siciliano et al., 2004) and thereby acts to transport and sequester Hg (Siciliano et al., 2004). Moorhead and Callaghan (1994) found that in contrast to reported inhibition effects of UV-B radiation on biotic decomposition of litter, direct exposure of litter to enhanced UV-B could increase its decomposition rates. Therefore, decomposition of non-living organic matter can be accelerated when UV-B photo-degrades surface litter, or retarded when the dominant UV-effect involves changes in the chemical composition of living tissues that reduce the bio-degradability of buried litter, or when microbes involved in the decomposition process become inhibited. These changes in decomposition rates could affect cycling of organic matter bound-contaminants such as metals, including Hg. The transfer of this decomposing organic matter from the watershed to surface waters would impact both physical and biochemical aspects of aquatic systems. Indeed, most phenolic and aromatic-based humic compounds found in inland waters are of terrestrial origin (Wetzel et al., 1995).

As stated earlier, in aquatic systems, dissolved organic matter originates from either planktonic photosynthesis, a process that is dominant in the open Ocean, or/and from external sources, which are dominant in inland waters. The effect of natural organic matter on the bioavailability and toxicity of metals has long been recognized. Thus Hg in natural systems, the relationship between Hg levels/accumulation and DOC are complex.

For instance, strong positive relationships have been reported between Hg and DOC (e.g., Watras et al., 1998; Cai et al., 1999), and data from previous investigations conducted in several Hg contaminated and non-contaminated riverine systems confirm the above observation (Figure 5-1) (Bonzongo et al., 1996a, Bonzongo et al., 1997; Lechler et al., 2000, Green, 2000). In the case of Figure 5-1, and although scattered, the data indicate the strong tendency of Hg to associate with organic matter in aquatic systems.

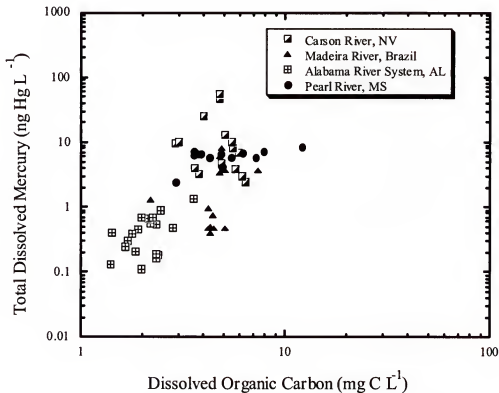


Figure 5-1. Dissolved total mercury versus dissolved organic carbon (DOC) in surface waters of four different river systems with different Hg levels (n = 60) (Bonzongo and Donkor, 2003).

In addition, several field studies have suggested that the formation of DOC-Hg complexes reduce the bioavailability of Hg to aquatic organisms (e.g., Grieb et al., 1990; Driscoll et al., 1995; Watras et al., 1998; Guo et al., 2001; Siciliano et al., 2004). In most drainage lakes, it is indeed true that a positive relationship could be observed between

methyl-Hg and DOC, and this is believed to arise from the fact that both DOC and methyl-Hg are produced in upstream wetlands. However, in seepage lakes, where in-lake processes produce methyl-Hg an inverse relationship is observed (Miskimmin et al., 1992). This is explained by DOC's effect on the availability of ionic Hg for methylation. Another observation is a dilution effect whereby high DOC is usually related to more productive aquatic systems where dilution of methyl-Hg per aquatic biomass occurs. Surprisingly, increases in Hg levels in fish tissues with increasing concentrations of humic substances in water have been also reported (Håkanson et al., 1990; Driscoll, 1995; Watras et al., 1998). Possible explanations for these trends can probably be found in the supply and conversion of different Hg forms, but such relationships are difficult to resolve based on field data alone (Sjöblom et al., 2000). For instance, recent laboratory studies showed that aquatic organisms can directly uptake nutritious low molecular weight organic compounds (Guo et al., 2000; Leaner and Mason, 2001). Since trace metals such as Hg are often associated with these carbon sources, it is then possible that Hg content of biota increases with the increase in the low molecular weight organic matter (LMWOM). *Therefore, one can speculate that UV-induced breakdown of recalcitrant organic matter to smaller organic compounds could speed up the bioaccumulation of Hg and its subsequent transport and sequestration.*

### **5.2.2 Direct Impact of UV-Radiation on Organic Matter**

Francko (1990) reviewed literature focusing on the effects of solar radiation on the bioavailability of dissolved organic matter. He reported that upper layers of the ocean and lakes are sites of UV-B induced stress to phytoplankton communities and complicated interactions between NOM and UV-B radiation, while aquatic photosynthetic organisms differ substantially in their tolerances to UV-B radiation exposure and changes in the

ratio UV-B/UV-A/PAR. In fact, a variety of photochemical reactions that could have important ramifications with respect to the cycling of carbon and other elements occur in natural waters. Kieber et al. (1989) postulated that LMWOM and biologically labile compounds are photochemically formed from the biologically refractory or non-utilizable portion of dissolved organic matter. Further investigations confirmed the role of UV in the production of dissolved LMWOM (Wetzel et al., 1995; Anesio et al., 2000). It is now known that photoproducts of the biologically refractory dissolved organic matter (DOM) in natural waters are not limited to LMWOM (e.g. formaldehyde, acetaldehyde, and the alpha-keto-acid, glyoxylate), but do include dissolved inorganic carbon (DIC); trace gases (CO and COS); and many other unidentified species. Miller and Zepp (1995) identified DIC as the major sink following the photo-degradation of DOM derived from a coastal estuary and two rivers. They also found that the formation rate of DIC is at least 2 orders of magnitude greater than that of the other photo-degradation products. Overall, their findings suggest that a total mineralization of organic matter could occur following a simple exposure to UV radiation. This would release any NOM-bound Hg; therefore, limiting the lifetime of biologically refractory compounds (Mopper et al., 1991; Wetzel et al. 1995; Siciliano et al., 2004; O'Driscoll et al., 2004), and likely, impacting the cycling and toxicity of Hg.

With regard to microorganisms, UV-radiation reduces the growth of bacterioplankton in upper layers of water bodies (e.g., Kaiser and Herndl, 1997). As a consequence, UV radiation indirectly retards the biological breakdown of any photo-produced labile organic matter in the photic layer, allowing the formed LMWOM to sink and undergo decomposition in deeper layers, where microbial activity remains normal

(Kaiser and Herndl, 1997). The release of organic matter-bound-Hg in deep water layers and at the water-sediment interface, where the depletion of dissolved oxygen is driven by the decomposition of non-living organic matter would then favor the bio-transformation of Hg by anaerobic microbial processes to produce the most toxic and readily bio-available methyl-Hg. Experimental evidence suggests that microbially-catalyzed Hg transformations play a key role in the biogeochemical cycling of Hg (Compeau and Bartha, 1985; Berman and Bartha, 1986; Barkay, 1992; Gilmour et al., 1992; Bonzongo et al., 1996b; Chen et al., 1997; Marvin-Dipasquale et al., 2001), and Hg compounds introduced into natural environments are transformed by bacteria involved in the decomposition of organic matter (Oremland et al. 1991; 1995; Gilmour and Henry, 1991; Gilmour et al. 1992; Marvin-Dipasquale and Oremland, 1998; Marvin-Dipasquale et al., 2000; King et al. 2001). Other reports indicate that the contribution of abiotic processes cannot be ruled out (Siciliano et al., 2004; O'Driscoll et al., 2004). The above observations suggest that a link probably exists between the effect of UV-radiation that is pronounced in upper layers of water bodies and dark reactions that take place in deep layers, away from solar radiation. If so, an exacerbation of such processes could be expected as a consequence of increasing solar UV-B radiation reaching the earth's surface.

### **5.2.3 Increasing Solar UV-Radiation and Hg Bioaccumulation/Toxicity**

Aquatic organisms are exposed to Hg through uptake from the aqueous phase, indirect uptake through food, or both (Sjöblom et al., 2000). Several physicochemical parameters control Hg bioaccumulation, hence, its toxicity to aquatic biota. These parameters include but are not limited to pH, temperature, Hg loading rates, rates at which Hg is removed from the environment, productivity and trophic position, and DOC.

In addition, primarily dissolved organic compounds, which are essentially mixtures of humic and fulvic acids of different molecular weights that can physically and chemically be affected by solar radiation. These are formed from decaying products of both in situ primary productivity (autochthonous), and mostly, terrestrial plants (allochthonous); dissolved organic matter can bind metals through chelation involving neighboring carboxyl and phenolic groups or sulfur groups (Strohal and Huljev, 1971; Morel, 1983; Stumm and Morgan, 1996; Siciliano et al., 2004). The binding between Hg and  $-SH$  groups is so strong that it allows Hg-humic complexes to dominate mercury speciation in freshwater (Allard and Arsenie, 1991; Hintelmann et al., 1995; 1997; Meili, 1997). In two recent studies, Guo et al. (2001) found that Hg bioaccumulation in oysters was inhibited in the presence of high molecular weight humic substances; while both Guo et al (2001) and Leaner and Mason (2001) reported an increased Hg bioaccumulation by aquatic organisms when dissolved organic matter was made of LMWOM only. These findings presupposed that the impact of UV radiation on dissolved organic matter results in increased Hg bioavailability. The hypothesis is that, in addition to increasing Hg availability to aquatic biota via direct uptake, increasing UV-B radiation could favor the formation of Hg-LMWOM complexes. The latter would then either be directly taken up by aquatic organisms or undergo a much faster oxidation in deepwater layers (or at the water-sediment interface) where Hg methylation co-occurs with organic matter degradation. Produced methyl-Hg would then find its way into the food chain.

### **5.3 Potential Impacts of UV-Radiation on Hg Cycling**

Photochemical reactions of DOM in surface layers of aquatic systems produce dissolved gasses that are supersaturated with respect to an equilibrium state with observed atmospheric concentrations. This imbalance drives the flux of gaseous

photoproducts from the ocean to the atmosphere. With regard to Hg, the formation of  $\text{Hg}^0$  by photo-reduction of electrically charged species could result in a net flux from water to the atmosphere (Kim and Fitzgerald, 1986; Xiao et al. 1991; Mason et al. 1994; Amyot et al. 1994; 1997a; 1997b; Costa and Liss, 1999 and 2000; O'Driscoll et al., 2004), while recent report of photo-induced oxidation of aqueous  $\text{Hg}^0$  (Lalonde et al. 2001) balances the above mentioned flux and increases the concentration of electrically charge Hg-species. Photo-catalyzed reactions could also lead to both degradation and production of methyl-Hg in surface waters (Sellers et al., 1996; Siciliano et al., 2002, 2004). The following discussion will focus on different photo-catalyzed reactions, and how they do or could impact Hg cycling.

### 5-3.1 Photo-reduction

Reduction of aqueous  $\text{Hg}^0$  by UV-radiation has been the subject of several studies (e.g. Amyot et al. 1994, 1997a, 1997b, Lalonde et al. 2001; Siciliano et al., 2004; O'Driscoll et al., 2004), and the results suggest that the significance of photo-induced reduction of  $\text{Hg}^0$  could vary with geographical locations, the DOC content of water bodies, and probably several other site-specific parameters. The main differences observed in evasion fluxes, when experiments are conducted under fluctuating solar radiation are pointed out. Studies conducted in North American temperate lakes showed that  $\text{Hg}^0$  evasion fluxes could vary from values as low as  $1.0 \text{ pmol m}^{-2} \text{ h}^{-1}$  to about  $11.4 \text{ pmol m}^{-2} \text{ h}^{-1}$  (e.g., Amyot et al. 1997a; Fitzgerald et al., 1994). In Ranger Lake for example, the flux of gaseous Hg increases rapidly after sunrise to reach peak values around noon, then decreases after noon to a minimum before sunrise (Amyot et al., 1997b). The similarity between this trend and fluctuations in total incident radiation observed by the same authors suggest that photo-induced processes are responsible for

most of the dissolved gaseous mercury (DGM) production, with the latter being mostly  $\text{Hg}^0$ . The role of increased solar radiation and UV-radiation output becomes important during summer when Hg fluxes increase, reaching values ten times greater than those observed during fall (Amyot et al., 1997a). With regard to this latter observation, warmer water temperature characteristic of summer periods could contribute increased Hg fluxes. In high Arctic lakes, the rate of the formation of DGM is controlled by: (1) the intensity of solar radiation and (2) the concentration of available photo-reducible  $\text{Hg}^{2+}$ -complexes (Amyot et al., 1997b). In this case, sample exposure to different portions of the electromagnetic spectrum (i.e. presence of solar radiation (transparent bottles), absence of solar radiation (black bottles), absence of UV-B (transparent bottles wrapped in mylar), absence of UV radiation (transparent bottles wrapped in UV filters model 226), has shown that UV-B alone accounted for 64 to 97% of DGM production in the two tested lakes, and 33% in a Arctic wetland setting. Finally, in these Arctic aquatic systems, the production of DGM was observed over a wide range of pH (5.7 – 8.3), and evasion fluxes ranged from 0.4 to 2.8  $\text{pmol m}^{-2} \text{h}^{-1}$ .

One potential consequence of increased  $\text{Hg}^0$  evasion from water bodies in low to mid-latitudes could be the increase in global dispersal of elemental-Hg, hence resulting in contamination of pristine regions. Numerous studies have shown that polar regions for instance are exposed to airborne contaminants such as volatile metalloids (e.g., Se, As), certain trace metals (e.g., Pb, Hg), and other substances (e.g., Persistent Organic Pollutants) (Haygarth and Jones, 1992; Iverfeldt et al., 1995; Pacyna and Keeler, 1995; Landers et al., 1995; Lockhart et al., 1995; Wania and Mackay, 1996; Schroeder et al., 1998). These contaminants are subject to long-range atmospheric transport before being



deposited on terrestrial and/or aquatic landscapes. Wania and Mackay (1996) reported that many “Persistent Organic Pollutants” (POPs) are volatile enough to cycle among air, water, and soil. In this case, warm temperatures would favor evaporation in mid-latitude regions, while cool temperatures at higher latitudes would favor deposition. It is suggested here that Hg could be subjected to such a global distillation process, and if so, it would probably behave like POP, in that, it would migrate to higher latitudes with time. Based on the vapor pressure of Hg (0.0012 mm at 20°C) and the above-described criterion of Wania and Mackay (1996) for POPs, increased  $\text{Hg}^0$  fluxes produced by photo-reduction at low to mid-latitudes could travel polar ward, where it would then accumulate. In fact, numerous studies have already pointed out that the atmosphere is the main route to introducing Hg to northern Polar Regions (Iverfeldt et al., 1995; Pacyna and Keeler, 1995; Landers et al., 1995; Lockhart et al., 1995). Finally, recent investigations of co-variation of Hg and ozone during tropospheric ozone depletion events after polar sunrise point to photocatalytically produced bromine and its reaction with  $\text{Hg}^0$  as the cause for the observed  $\text{Hg}^0$ -depletion. The result is production of reactive Hg, which is removed from the atmosphere and deposited on polar terrestrial/aquatic landscapes (Lindberg et al., 2001; Lu et al., 2001). Accordingly, solar radiation, namely UV-B, could lead to the introduction of bioavailable Hg species into the biosphere. Unfortunately, introduction of this reactive Hg to terrestrial and aquatic landscapes occurs at a time biological activity peaks up (Steffen et al., 2002). In conclusion, one should anticipate the solar radiation driven aspect of Hg cycling to become significant with increasing solar UV-B output.

### 5-3.2. Photo-oxidation

If photo-reduction of Hg is by far the most investigated process, it is not the only photo-induced process that takes place in surface waters. Lalonde et al. (2001) suggest that photo-oxidation of  $\text{Hg}^0$  co-occurs with photo-reduction in surface waters. Considering a piston velocity of  $1\text{ m d}^{-1}$ ,  $\text{Hg}^0$  aqueous concentration of  $0.2\text{ pM}$ , and assuming a negligible atmospheric Hg concentration, they calculated a volatilization flux out the water column of  $7\text{ pmol m}^{-2}\text{ h}^{-1}$ . By comparison, losses of  $\text{Hg}^0$  due to its photo-oxidation ranged from:  $15\text{ pmol m}^{-2}\text{ h}^{-1}$  to  $40\text{ pmol m}^{-2}\text{ h}^{-1}$  in fresh and sea waters, respectively. The authors concluded that: *“photo-oxidation of  $\text{Hg}^0$  is likely to dominate during summer days as compared to volatilization of  $\text{Hg}^0$ ”*

One should note, however, that a large degree of uncertainty is associated with the transfer velocity used in these flux calculations, which fluctuates widely as a result of changes in wind speed. Also, assumed values of transfer velocity give only gross estimates of fluxes. So, assuming a dominance of photo-oxidation of  $\text{Hg}^0$  over  $\text{Hg}^0$ -volatilization, photo-produced electrically charged Hg species could increase, or at least maintain, the pool of bioavailable Hg.

### 5.3.3 Direct Effect of Solar Radiation on Aqueous Methyl-Hg-Degradation and Hg-Methylation

Sellers et al. (1996), obtained data from in-lake incubations showing that photo-degradation of methyl-Hg occurs, and that photo-degradation rates decreased with depth from about  $25\text{ pg l}^{-1}\text{ d}^{-1}$  in Lake Surface to below detection at depth of about 5m. Siciliano et al. (2002) have also confirmed the photo-degradation of methyl-Hg in surface waters. Moreover, this second study also found that concentrations of methyl-Hg peak in surface waters at noon, and in such instances, microbial inhibitors would not prevent Hg

methylation. Further, their data showed a positive correlation between methyl-Hg concentrations and sunlight, and emphasized the importance of DOC in abiotic photochemical production of methyl-Hg. Lately, Siciliano et al. (2004) demonstrated that the photoproduction of MeHg is dependent on DOM concentrations and type and that, concentrations of MeHg increased during daylight hours.

Overall, the above observations point to the occurrence of abiotic methyl-Hg degradation and Hg-methylation driven primarily by solar radiation. However, more studies are still needed to establish the mass balance between the two concurrent processes of degradation and methylation, and then, predict the consequence of increasing UV-B radiation.

#### **5.4 Preliminary Laboratory Study to Assess the Indirect Effect of UV-B on Hg Transformation**

Wetzel et al. (1995) demonstrated that UV-B induced breakdown of high molecular weight organic matter (HMWOM) results in formation of lower molecular weight organic matter (LMWOM) moieties. Unfortunately, there are no data in the literature on how the above effect of UV could affect the fate of Hg in subsequent dark reactions. To assess this indirect effect of UV-B radiation on Hg cycling, a set of laboratory experiments was conducted.

##### **5.4.1 Methods**

For laboratory assays, sediments with a total-Hg concentration of 120 ppb ( $\text{ng g}^{-1}$ ) were collected from a “pristine wetland” near the city of Gainesville, FL and used as a source of Hg-methylating microorganisms in slurries. Before slurry preparation, the sediment was sieved (0.5mm), yielding homogeneous fine materials. Sieved sediment was then used to prepare slurries by dilution in DI-water (1:10; mass per volume). In

addition to non-spiked samples, a duplicate set of slurries was spiked with: (1) humic substances only (obtained from Sigma-Aldrich); (2) humic substances previously treated with  $\text{HgCl}_2$  and added to the slurry to give a final concentration of 400ng Hg/ml of slurry; and finally (3), UV-B pre-treated humics, spiked later with  $\text{HgCl}_2$  and added to the slurry to give a final Hg concentration of 400ng Hg/ml of slurry. Samples were incubated in the dark, and Hg-methylation in incubation vials was stopped after 24, 48, 72, and 96 hours. At the end of the incubation period, samples were acidified and frozen. Methyl-Hg was later extracted from slurries using the alcoholic/alkaline digestion technique, and analyzed by CV-AFS following derivatization, GC separation, and thermo-decomposition (Bloom, 1989).

#### 5.4.2 Results and Discussion

The results, corrected from the non-spiked samples, are presented in Figure 5-2. They show a clear difference in rates of methyl-Hg production under the three tested conditions. In general, Hg bound to UV-B treated humic would become more prone to microbial methylation (methyl-Hg production rate up to  $0.33\text{ng ml}^{-1}\text{h}^{-1}$ ) than the fraction bound to non-irradiated humics ( $0.041\text{ng ml}^{-1}\text{h}^{-1}$ ). These data suggest that UV-B could indirectly speed up the production of methyl-Hg by (1) breakdown of HMWOM to produce LMWOM; and (2) photo-oxidation of  $\text{Hg}^0$  to produce  $\text{Hg}^{2+}$ . Binding of photo-oxidized  $\text{Hg}^0$  to LMWOM would then undergo dark reactions leading to methyl-Hg formation, if the newly formed complexes reach the anoxic region of an aquatic system.

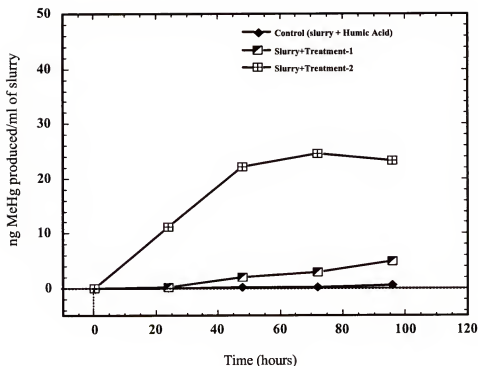


Figure 5-2. Methylmercury production in anoxic sediment slurries spiked with (1) humic substances (control); (2) humic-Hg complexes (HMWOM) without UV-B pretreatment (*treatment 1*); and (3) humic-Hg complexes formed after pretreatment of humic substances with UV-B (LMWOM) (*treatment 2*).

### 5-5 Summary

Figure 5-3 summarizes some hypothetical pathways for aqueous Hg, initially bound to NOM and after the NOM-Hg complexes have been exposed to UV radiation.

Photochemical breakdown of such NOM-Hg complexes would release several photoproducts including:

- Organic matter of lower molecular weight (LMWOM)  $\text{Hg}^{n+}$  and Hg bound to ligands (L), such as the newly formed LMWOM, to give complexes in the form  $\text{HgL}_x^{n+}$ . A fraction of  $\text{HgL}_x^{n+}$  produced in top water layers could escape further photochemical and/or microbial transformations at the surface, and progressively sink to deep and dark aqueous layers where the release of Hg from binding ligands and its subsequent transformation would be linked to microbial degradation of organic matter. Hg methylation would occur and formed methyl-Hg would then (1) find its way into the food chain; (2) undergo microbial demethylation; or (3) diffuse back to the overlaying water where it could become either bio-accumulated or as shown by Sellers et al. (1996), simply photo-transformed following

exposure to incoming solar UV radiation. This photo-degradation would be balanced, and perhaps exceeded, by the photo-induced methylation of dissolved Hg-complexes.

- Photoproducts such as dissolved inorganic carbon (DIC) and radicals, and trace gases, including gaseous mercury ( $\text{Hg}^0$ ) formed via photo-reduction of released  $\text{Hg}^{2+}$ . As mentioned earlier, the photo-reduction of Hg has been investigated through laboratory and field studies (e.g. Allard and Arsenie, 1991; Schroeder et al. 1992; Nriagu, 1994; Amyot et al., 1994; Xiao et al., 1994 and 1995; Beucher et al., 2002), and from a theoretical standpoint, at pH greater than ~5.5, which is the case for most natural waters,  $\text{Hg}^{2+}$  can undergo reduction to  $\text{Hg}^0$  by reacting with hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), which is a known product of photolysis reactions involving humic substances (Schroeder et al. 1992). At pH less than 5.5, which is often the case for waters that are either impacted by acidic pollution or naturally, containing very large amounts of DOC, the oxidation of  $\text{Hg}^0$  rather than reduction of  $\text{Hg}^{2+}$  would occur as described by Schroeder et al. 1992.

Lastly, Ghana is located in the tropics and its proximity to the equator implies intense solar radiation. Naturally high solar radiation levels in the tropics are very common (Whitefield et al., 2000; Diaz et al., 2000). Warm temperatures, high annual precipitation, high organic rich soils and sediments, and intense microbial activity characteristics of most tropical regions would favor the oxidation of  $\text{Hg}^0$  by biotic and abiotic transformations. Produced  $\text{Hg}^{2+}$  bound to OM becomes less bioavailable to methylating microbes. Solar radiation would accelerate the breakdown of some high molecular weight OM, releasing low molecular weight bound Hg complexes that are easily degraded by microbial driven oxidation processes. Hence, in Hg-contaminated tropical ecosystems such as those found in Ghana or other artisanal mining regions of Africa and South America, solar radiation is likely to accelerate the cycling and transformation of Hg in organic rich environments. Additional studies employing photochemistry to investigate and assess the role of solar radiation on the fate of Hg cycling in aquatic and terrestrial systems due to mining operations are warranted.

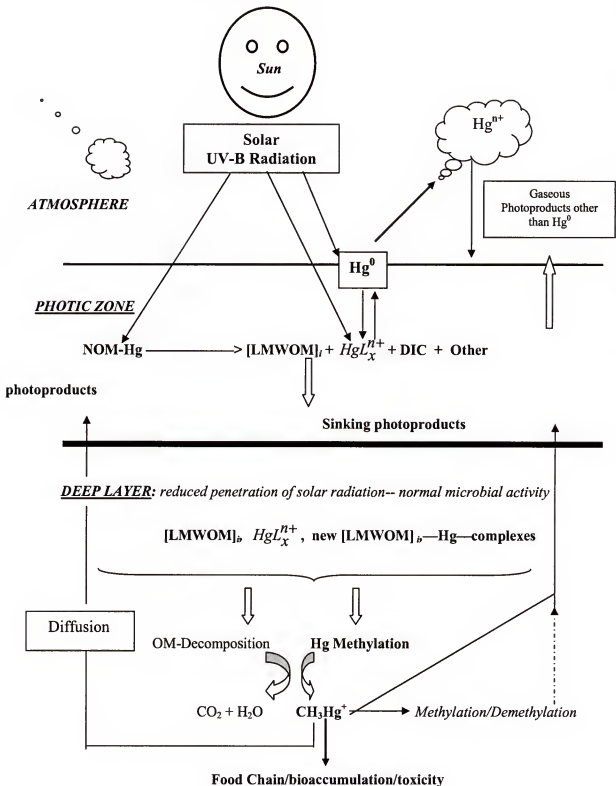


Figure 5-3. A simplified diagrammatic representation of the fate of photo-products of NOM-Hg complexes (L = ligands other than produced labile NOM ( $[\text{NOM}]$ );  $[\text{LMWOM}]_i$  = low molecular weight organic matter produced from the photo-degradation of NOM).

## CHAPTER 6 CONCLUSIONS AND RECOMMENDATIONS

### 6.1 Conclusions

The following conclusions are drawn from this research investigation:

- The obtained data showed rather low total concentrations for both Hg and other trace metals (e.g. Pb, As, V, Zn, Co, Cu) as compared to other well studied mining impacted aquatic systems worldwide despite the reported long-term gold mining activities characteristics of the studied area.
- The determination of the enrichment factor (EF) for these metals indicated that sediment pollution in the Pra River System has a cyclic trend, with contamination signs observed only during the rainy season for Hg, Zn, and to some extent As.
- This tropical river system appears to have a self-cleansing process; Hg introduced in the river is predominantly transported downstream and levels observed in sediments are usually within the accepted global background range.
- The Pra River system receives most of its Hg pollution during the dry season due to increased gold mining activities.
- The analysis of the few fish and hair samples obtained indicated Hg had entered the food chain.
- There is a great potential for methyl-Hg formation and accumulation in both surface soils and sediments of the Pra River basin, and Hg-contaminated soils seem to represent the hot spots for methyl-Hg formation that is driven primarily by the increase in soil water content during the rainy season.
- Storm water run-off and likely rain infiltrating water act as vehicle to transport different Hg species including methyl-Hg from soils to nearby waterways via inputs to surface waters and/or discharges from groundwater.
- The intense solar radiation characteristics of the tropics could play a key role in stimulating methyl-Hg formation by accelerating the breakdown of recalcitrant organic matter and rendering the inorganic Hg bound to them bio-available to methylating microbes.



## 6.2 Recommendations

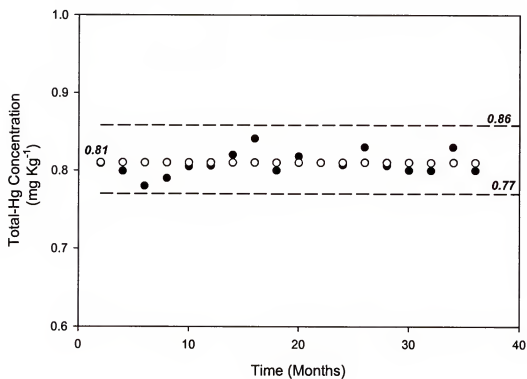
The following recommendations are made to further the extent of knowledge of Hg biogeochemistry in the Pra River Basin:

- This study points to the river delta and estuary as depositional areas and further studies on the fate of Hg in the Pra River system should focus on these terminal basins, where Hg transformations and bioaccumulation could impact the intense commercial fishing in these specific areas. Additionally, a more comprehensive investigation of Hg in fish tissues (dry and fresh) embracing spatial and temporal variations and more trophic levels are required.
- In Hg contaminated tropical ecosystems such as those found in Ghana or other artisanal mining regions of Africa and South America, solar radiation is likely to accelerate the cycling and transformation of Hg in organic rich environments. Therefore additional studies employing photochemistry to investigate and assess the role of solar radiation on the fate of Hg cycling in aquatic and terrestrial systems due to mining operations are warranted.

APPENDIX A  
QA-QC FOR THE SEDIMENT AND SOIL ANALYSES FROM THE PRA RIVER  
BASIN

**A.1 Total-Hg**

Trends of Total-Hg recovered from a standard reference material (IAEA 405) with a certified average  $0.81 \text{ mg Hg Kg}^{-1}$ . The dashed lines show the upper and lower certified values. The open circles are the certified average values and the blacked dotted circles are the calculated or found values for the reference material.



## A.2 Methyl-Hg

Trends of Methyl-Hg recovered from a standard reference material (IAEA 405) with a certified average  $0.00549 \text{ mg Hg Kg}^{-1}$ . The dashed lines show the upper and lower certified values. The open circles are the certified average values and the blacked dotted circles are the calculated or found methyl-Hg values for the reference material.

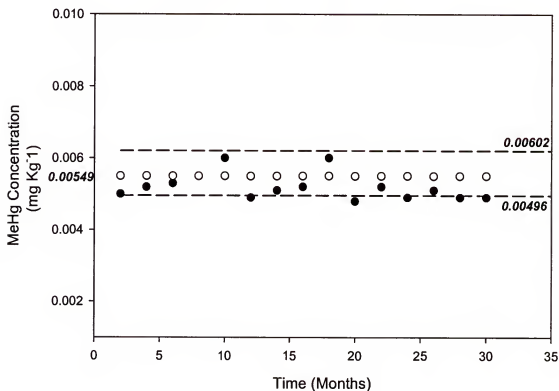




Table A-1. Continued  
River

Section	Site #	Season	Na+	K+	Mg2+	Ca2+	Cl-	SO42-	NO3-	NO2-	PO43-	T(oC)	pH	DOC
	8	Wet	9.46	5.80	5.02	23.22	4.61	4.16	1.64	BDL	BDL	23.5	6.26	11.07
		Dry	7.60	5.35	2.05	13.64	0.40	4.18	1.80	13.20	198.70	26.0	6.94	6.67
Offin	9	Wet	12.16	8.15	5.47	12.45	7.95	7.66	2.35	BDL	BDL	24.0	6.05	12.58
		Dry	10.00	8.30	5.17	21.00	0.28	5.17	1.34	14.60	206.10	26.5	6.38	7.84
10		Wet	14.20	7.80	5.58	12.78	6.18	10.74	2.06	BDL	BDL	23.5	6.55	16.79
		Dry	15.72	8.30	5.17	28.00	0.45	6.56	1.35	11.54	188.00	26.0	6.13	7.23
11		Wet	13.49	8.94	6.48	14.58	7.13	8.30	2.31	BDL	BDL	24.0	6.13	14.46
		Dry	15.41	7.76	5.59	28.60	0.59	33.20	1.21	23.10	200.10	26.0	6.40	7.65
12		Wet	17.06	24.57	19.65	25.42	6.56	6.56	5.02	BDL	BDL	24.0	6.25	5.71
		Dry	107.60	26.84	51.60	180.10	0.29	38.60	1.20	16.22	209.60	26.5	6.89	6.65
13		Wet	17.40	8.33	5.60	11.80	5.38	7.44	1.96	BDL	BDL	24.0	6.45	13.82
		Dry	19.21	8.91	7.03	34.62	21.93	319.60	20.50	2.10	149.20	26.0	6.90	7.50
14		Wet	9.83	7.26	5.05	11.00	5.54	6.70	2.73	BDL	BDL	24.0	6.27	7.12
		Dry	15.40	8.77	5.91	27.90	1.49	49.36	2.18	16.36	145.60	26.0	6.85	7.64
15		Wet	17.40	11.19	3.66	5.31	6.97	3.42	4.76	BDL	BDL	23.5	6.53	10.88
		Dry	5.16	3.02	1.65	4.15	0.59	32.70	1.36	18.74	192.90	26.5	7.15	3.14

Table A-1. Continued

River		Site	Season	Na+	K+	Mg2+	Ca2+	Cl-	SO42-	NO3-	NO2-	PO43-	T(OC)	pH	DOC
		Section #													
Upper	Pra	16	Wet	9.92	7.61	3.29	8.72	5.75	1.31	0.89	BDL	BDL	24.0	6.62	15.31
			Dry	5.77	3.00	1.71	11.47	0.20	3.72	0.04	8.11	184.10	25.0	7.42	6.74
		17	Wet	3.77	6.35	3.73	7.73	3.17	3.06	2.13	BDL	BDL	24.0	6.40	10.08
			Dry	6.48	3.41	2.32	15.71	0.48	0.25	0.06	6.23	144.20	25.0	7.68	6.78
	18	Wet	10.50	9.16	7.10	3.53	2.70	1.18	1.18	0.87	BDL	BDL	24.0	6.28	9.37
			Dry	5.64	2.01	1.49	7.58	0.48	0.65	0.20	8.23	153.60	26.0	7.42	6.91
	19	Wet	8.40	5.81	4.61	3.93	4.52	4.82	4.82	10.23	BDL	BDL	24.0	6.76	4.46
			Dry	14.60	3.43	2.20	1.99	0.16	1.30	0.10	7.58	194.50	26.0	7.10	11.61
	20	Wet	8.10	16.78	4.80	4.45	3.37	1.52	1.14	BDL	BDL	BDL	23.5	6.65	10.11
			Dry	83.76	7.94	7.36	12.50	0.32	0.84	0.29	10.34	187.80	26.0	7.72	6.74
	21	Wet	13.20	6.89	3.21	6.00	3.74	1.23	1.23	6.15	BDL	BDL	24.0	7.70	8.33
			Dry	4.10	2.06	1.39	8.32	0.32	1.13	0.01	15.10	196.50	26.0	7.20	6.17

APPENDIX B  
TOTAL MERCURY (THg) CONCENTRATIONS ( $\text{ng g}^{-1}$  DRY WEIGHT) AND  
PERCENTAGE OF SPECIES CONTRIBUTION IN THE INVESTIGATED  
SEDIMENTS

Table B-1. Total mercury (THg) concentrations (ng g<sup>-1</sup> dry weight) and percentage of species contribution in the investigated sediments

Site #	F1	F1	F2	F2	F3	F3	F4	F4	F5	Amount Extracted ng g <sup>-1</sup>	Amount Before Extraction ng g <sup>-1</sup>	% Extracted
	CH <sub>3</sub> COOH+ HCl ng g <sup>-1</sup>	%	KOH ng g <sup>-1</sup>	%	HNO <sub>3</sub> ng g <sup>-1</sup>	%	Aqua Regua ng g <sup>-1</sup>	%	HF + HCl + HNO <sub>3</sub> ng g <sup>-1</sup>	%		
Lower												
Pra	1.35	27.11	2.01	40.36	0.70	14.06	0.31	6.22	0.61	12.25	4.98	62.25
2	3.34	25.83	5.64	43.62	1.64	12.68	1.06	8.20	1.25	9.67	12.93	76.06
4	5.44	16.29	21.4	64.09	2.51	7.52	2.76	8.27	1.28	3.83	33.39	77.65
6	1.41	18.83	3.83	51.13	1.06	14.15	0.78	10.41	0.41	5.47	7.49	83.32
8												
River												
Offin												
10	1.11	22.61	1.41	28.72	0.73	14.87	0.96	19.55	0.7	14.26	4.91	70.14
12	6.58	33.17	10.78	54.33	0.82	4.13	0.58	2.92	1.08	5.44	19.84	76.31
Upper												
Pra												
17	0.74	21.96	1.58	46.88	0.36	10.68	0.28	8.31	0.41	12.17	3.37	67.40
19	9.66	27.89	18.87	54.47	1.66	4.79	1.87	5.40	2.58	7.45	34.64	80.56



APPENDIX C  
MERCURY METHYLATION AND METHYLMERCURY DEMETHYLATION  
IN SEDIMENTS

River Offin Site 4

Hg Methylation			MeHg Demethylation		
<u>Time (Hrs)</u>	<u>MeHg ng/g</u>	<u>SD</u>	<u>Time (Hrs)</u>	<u>MeHg ng/g</u>	<u>SD</u>
0	0	0	0	10	0
60	7.3	0.08	60	3.82	0.19
72	4.8	0.03	72	5.35	0.38
84	3.8	0.78	84	11.36	1.86
96	4.3	0.47	96	5.9	0.12

River Offin Site 6

Hg Methylation			MeHg Demethylation		
<u>Time (Hrs)</u>	<u>Mean ng/g</u>	<u>SD</u>	<u>Time (Hrs)</u>	<u>Mean ng/g</u>	<u>SD</u>
0	0.59	0.01	0	10.59	0
60	24.05	13.43	60	14.15	1.34
72	26.6	5.05	72	8.17	0.91
84	27.09	3.99	84	11.81	2.11
96	18.2	2.28	96	17.43	1.81

## Lower Pra Site 2

Hg Methylation			MeHg Demethylation		
<u>Time (Hrs)</u>	<u>Mean ng/g</u>	<u>SD</u>	<u>Time (Hrs)</u>	<u>Mean ng/g</u>	<u>SD</u>
0	0.46	0.15	0	10	0
60	6.11	0.72	60	1	0.37
72	3.78	0.66	72	2.98	0.41
84	12.25	0.1	84	7.2	1.01
96	17.78	3.65	96	7.96	2.85

## Lower Pra Site 3

Hg Methylation			MeHg Demethylation		
<u>Time (Hrs)</u>	<u>Mean ng/g</u>	<u>SD</u>	<u>Time (Hrs)</u>	<u>Mean ng/g</u>	<u>SD</u>
0	0	0	0	10	0
60	17.02	4.25	60	3.6	0.21
72	9.35	2.41	72	7.51	0.47
84	14.87	2.79	84	7.24	1.65
96	10.5	1.31	96	9.02	1.59

## Lower Pra Site 6

Hg Methylation			MeHg Demethylation		
<u>Time (Hrs)</u>	<u>Mean ng/g</u>	<u>SD</u>	<u>Time (Hrs)</u>	<u>Mean ng/g</u>	<u>SD</u>
0	0.59	0.13	0	10.69	0.15
60	3.11	0.79	60	11.47	2.75
72	9.03	2.48	72	8.52	1.08
84	7.281	2.55	84	9.95	0.38
96	12.2	1.48	96	15.05	3.07

## Lower Pra Site 8

Hg Methylation			MeHg Demethylation		
<u>Time (Hrs)</u>	<u>Mean ng/g</u>	<u>SD</u>	<u>Time (Hrs)</u>	<u>Mean ng/g</u>	<u>SD</u>
0	0.59	0.13	0	10.69	0.15
60	20.28	3.57	60	13.69	2.46
72	22.04	0.24	72	6.65	2.32
84	22.27	0.66	84	9.19	2.22
96	35.5	2.27	96	15	2.79

## Upper Pra Site 19

Hg Methylation			MeHg Demethylation		
<u>Time (Hrs)</u>	<u>Mean ng/g</u>	<u>SD</u>	<u>Time (Hrs)</u>	<u>Mean ng/g</u>	<u>SD</u>
0	0	0	0	10	0
60	31.52	0.05	60	6.19	1.58
72	21.3	1.52	72	12.57	2.84
84	22.32	3.43	84	23.41	0.09
96	23.21	0.57	96	26.64	5.29

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## BIOGRAPHICAL SKETCH

Augustine was raised up in Obuasi, the single richest gold mining town in the world. He obtained his bachelor of honors in chemistry from University of Science and Technology, Kumasi, Ghana, in 1984. By dint of hard work, he was awarded Australian government scholarship to study Chemistry at Flinders University, Adelaide, South Australia, for the Master of Science degree, in 1989. He returned in 1992 and worked for the Ministry of Education and Kumasi Polytechnic and later joined Accra Polytechnic in 1995 to lecture and research.

Augustine joined the Department of Chemistry, the University of Florida in fall 1998 and completed a Master of Science degree in Fall 2000. That same year he transferred to the Department of Environmental Engineering Sciences to continue his doctor of philosophy program.

He is married to Alice Donkor (Mrs.), a professional caterer, and they are blessed with three children, Glory (boy), Joy (girl) and Peace (girl).

This dissertation was submitted to the Graduate Faculty of the College of Engineering and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

May 2005

A handwritten signature in dark ink, appearing to read "Pramod P. Khargonekar", is positioned above a horizontal line.


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Pramod P. Khargonekar  
Dean, College of Engineering

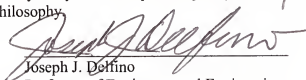
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Kenneth Gerhardt  
Interim Dean, Graduate School

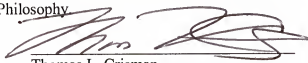
I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

  
Jean-Claude J. Bonzongo, Chairman  
Assistant Professor of Environmental  
Engineering Sciences


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Joseph J. Deffino  
Professor of Environmental Engineering  
Sciences

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Thomas L. Crisman  
Professor of Environmental Engineering  
Sciences

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James Winefordner  
Professor of Chemistry Department